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 Meusel et al.

Anonymous Referee #1

General comments:

In this manuscript the authors present results of HONO and other trace gas species from a study performed in Cyprus as part of the CYPHEX campaign in 2014. During the measurement period they observed a high HONO/NOx ratio and a large daytime source of HONO. A budget analysis is performed and a missing source of HONO up to 3.4 x 10^6 molecules cm^{-3} s^{-1} calculated, which is comparable to values reported in mountain and forest sites. Under humid conditions the HONO source correlates well with NO and the authors attribute this missing HONO source to emissions from soil. Finally, the impact of the HONO on OH production rates is calculated and the results show that the HONO photolysis contributes, on average, 30% to OH production during the morning and evening.

Understanding the daytime source of HONO is important due to its role in OH formation and this study provides important data on HONO sources in a location which is not strongly impacted by combustion sources.

The manuscript is well written, with appropriate sections and easy to follow. I recommend the manuscript for publication in ACP after addressing the comments below:

Response:

We thank the reviewer for the positive evaluation and please find our point-to-point responses as listed below.

Specific comment:

One of the main concerns is that no uncertainty analysis has been performed for the HONO/NOx ratios or the HONO budget and calculation of the missing HONO sources. This should include instrument uncertainties in the HONO and NOx measurements along with errors in the PSS calculation. It would then be beneficial to include error bars on Figure 5a and b, to show the upper and lower limits to the estimated unknown HONO source.

Response:

Following the reviewer's suggestion, we now state all instruments' uncertainties in the revised manuscript. The uncertainty of LOPAP (HONO) is 10%, based on the uncertainties of gas and liquid flow rates, regression of the calibration curve, and calibration standard solutions (manual of LOPAP, QUMA 2004). The accuracy (2 sigma) of the OH measurements was 29% and the precision (1 sigma) was 4.8×10^5 molecules cm^{-3} (personal contact with Harder et al., hartwig.harder@mpic.de). The instrument uncertainties for NO, NO_2, O_3, J were already stated in the original manuscript (20%, 30%, 5%, 10%, personal contact with Fischer et al, horst.fischer@mpic.de and Crowley et al., john.crowley@mpic.de).

According to Gaussian error propagation, these instrument uncertainties affect the calculation of the unknown HONO source S_{HONO} with about 16%.

We agree that error bars would help to indicate the uncertainty of the source and sink terms in our calculations. As Fig. 5 a and b show half-hourly mean values of diurnal patterns, we prefer to show the standard deviation of the diurnal mean values as error bars, now included in Fig. 5 a and b, and to discuss the uncertainties in the text.

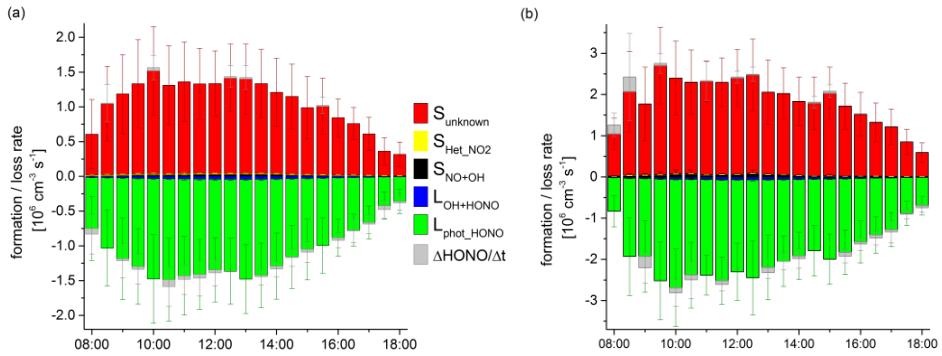
We now added in the revised versions of the manuscript:

page 4 line 13-15: "The accuracy of the HONO measurements was 10%, based on the uncertainties of liquid and gas flow, concentration of calibration standard and regression of calibration ."

page 4 line 36-37: "The accuracy (2 sigma) of the OH measurements was 29% and the precision (1 sigma) was 4.8×10^5 molecules cm^{-3}."

page 10 line 21-23: "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."

in Fig. 5a/b error bars based on standard deviation of diel mean values are added



Revised Fig. 5a+b including error bars; as suggested in another comment, the NO_2 conversion rate for the heterogeneous reaction in the dry case (b) is now adopted as suggested by the referee. (ΔHONO/Δt was added as discussed in a comment by reviewer 2)

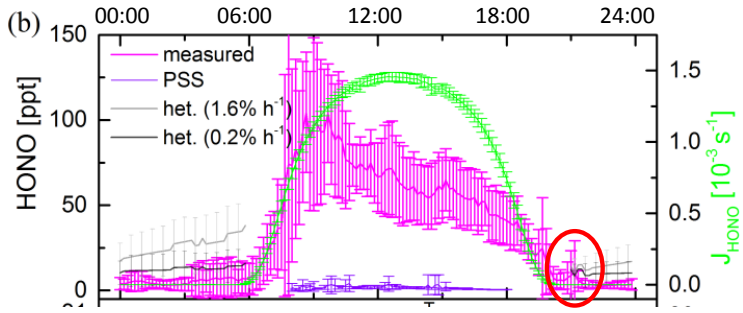
Specific comment:

In section 5.1, the heterogeneous reaction of NO_2 to form HONO is estimated by applying an NO2-HONO conversion rate of 1.6% h^{-1} overnight. Under humid conditions the estimated values agree well with measured values. A much lower rate of 0.22 % h^{-1} was applied in the drier period, which the author's state matches better to their observations. However, Fig 4. shows the measured HONO is still lower than the estimated values during some periods overnight. Perhaps it would be better to determine a conversion rate under dry conditions for this site using the NOx scaling approach (e.g. Sorgel et al., 2011) to compare with other studies, as I expect it is lower.

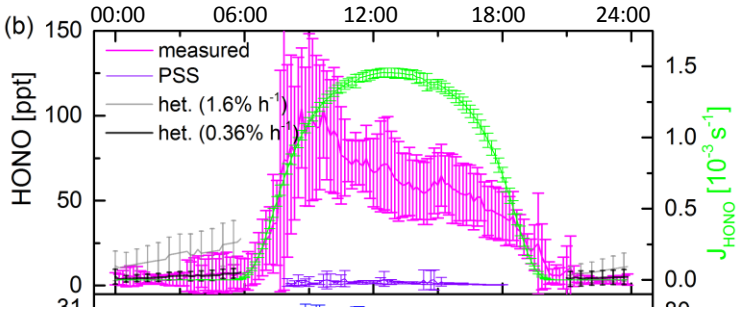
Response:

Thank you for this comment and suggestion. Accordingly, we now use the approach from Alicke et al., 2002+2003; Su et al. 2008b and Sörgel et al., 2011b for the conversion rate of the dry nights: $rate = \frac{HONO_{t2} - HONO_{t1}}{\Delta t * \overline{NO_2}}$. The respective average conversion rate is now 0.36% h^{-1}(slightly higher than the 0.22 % h^{-1} used before).

Also, a more representative HONO nighttime starting concentration 4.4 ppt is now used to better match the observations (as the original starting concentration 12.2 ppt was too high, the observed average concentration decreased afterwards, see marked area in old fig 4b).



Upper panel of old Fig. 4b,



Upper panel of revised Fig. 4b with adopted nighttime NO_2 conversion rate based on Soergel et al. (2011b) and a more representative HONO nighttime starting concentration. According to comment below, error bars are now in darker color.

The manuscript, section "5.1 nighttime HONO accumulation" on page 8 from line 15-33 is now revised to: "Instead, nighttime HONO concentrations can be estimated due to heterogeneous reaction of NO_2 described in Eq. (1) ***(Alicke et al., 2002+ 2003; Su et al., 2008b; Sörgel et al., 2011b).*** Three studies in different environments from a rural forest region in East Germany (Sörgel et al., 2011b) and a non-urban site in the Pearl River delta, China (Su et al., 2008b) to an urban, polluted site in Beijing (Spataro et al., 2013) found a conversion rate of ***about*** 1.6% h^{-1} ***(1.1-1.8 % h^{-1}).***

$$[HONO]_{het} = [HONO]_{evening} + 0.016\ h^{-1}[NO_2]\ \Delta t, \qquad \text{(Eq. 1)}$$

$[HONO]_{het}$ denotes the accumulation of HONO by heterogeneous conversion of NO_2, $[HONO]_{evening}$ the measured HONO mixing ratio at ***20:30*** LT, $[NO_2]$ the measured average NO_2 mixing ratio between ***20:30*** and 7:30 LT, Δt time span in hours.

Measured and calculated HONO mixing ratios are compared in figure 4 (upper panel). During the humid period, during night the estimated (according Eq. (1), fig. 4a upper panel, grey line) and observed HONO mixing ratios are in good agreement ($R^2 = 0.9$). During the drier period the observed HONO mixing ratios were lower than the ones calculated with a NO_2 conversion rate of 1.6% h^{-1}. ***Here the approach for the nighttime conversion frequency by e.g. Alicke et al., 2002+2003, Su et al., 2008b or Sörgel et al., 2011b ($rate = \frac{HONO_{t2} - HONO_{t1}}{\Delta t * \overline{NO_2}}$) was used. The 7 days average conversion rate for the dry nights was 0.36% h^{-1} (fig. 4b, upper panel, black line), comparable to results of Kleffmann et al. (2003) reporting a conversion rate of 6x10^{-7} s^{-1} (0.22% h^{-1}) for rural forested land in Germany***."

comments:

Pg 3, L25-26. Please state the uncertainty of the HONO measurements here too.

See comment above, the HONO uncertainty is now stated in this section.

Pg 6, L18. The ± values in the parenthesis should be clarified. Are these 1-sigma standard deviation of the mean?

Correct, this is now declared in the text on page 6 line 25: "…(± 25 pptv, 1σ standard deviation, following alike)"

Pg 7, L7. It is stated that the mean NO mixing ratios are close to the detection limit at 2 pptv, however, this is actually below the detection limit, which is given as 5 pptv on Pg 4, L13.

Sorry for this typo. Now the correct detection limit of 5 pptv of NO as written in the instrument description is now used here.

Pg 8, L5-7. Here, HONO mixing ratios are estimated and compared to the measured HONO overnight using a conversion factor between NO2 and HONO of 1.6% h^{-1}. The authors cite three studies where this value has been determined, although, it should be made clear here that a range of values were reported across these studies.

Correct. Now the range of values is stated in the modified version (see response on comment above) Sörgel et al. (2011) reported 1.1 (±0.65) % h^{-1}, Spataro et al. (2013) 1.5-1.8 % h^{-1} and Su et al. (2008) came up with a best estimate of 1.6 % h^{-1}, based on different scaling methods.

Pg 9, L25. Please state the values for k_1 and k_2 used in Eq. 2.

The rate constants k_1, k_2 (and k_3 and k_4) are temperature dependent, so stating only one value would not be appropriate. The respective formulas were taken from Atkinson et al. (2004), as was already cited in the original manuscript.

NO+OH -> $k_1 = 7.4 \times 10^{-31}(\frac{T}{300})^{-2.4}[N_2]$

HONO+OH -> $k_2 = 2.5 \times 10^{-12}\exp(\frac{260}{T})$

$NO+HO_2$ -> $k_3 = 3.6 \times 10^{-12}\exp(\frac{270}{T})$

$NO+O_3$ -> $k_4 = 1.4 \times 10^{-12}\exp(-\frac{1310}{T})$

E.g. at a temperature of 23°C, typical for the measurement time on Cyprus: $k_1 = 1.36\text{x}10^{-11}$ s^{-1}, $k_2 = 6.01\text{x}10^{-12}$ s^{-1}, $k_3 = 8.96\text{x}10^{-12}$ s^{-1}, $k_4 = 1.68\text{x}10^{-14}$ s^{-1}

In the revised manuscript the temperature dependence is now pointed out, and respective numbers are given for a typical daytime temperature on Cyprus during the campaign (23°C)

Fig 4: The error bars in figure 4b for the 0.2% rate are difficult to see, please use a darker color or use thicker lines.

Thanks for indicating. Fig 4b is now changed accordingly (see response on comment above).

In Figure 5, the caption states that a conversion rate of 1.6% h^{-1} is used for S_{Het_NO2} , however, Figure 4b shows that a lower rate (0.22% h^{-1}) is more appropriate for the dry period. Please clarify which rate you use for Fig 5b.

Correct. Indeed, in the original manuscript 1.6% h^{-1} was used for both by mistake. In the revised manuscript the conversion rate adopted by Soergel et al. (2011b) is now used (0.36% h^{-1}; see comment above), and the figure caption corrected accordingly. We thank the reviewer for exposing this critical detail.

Fig 6. Include units for NO_2 in the legend.

Thanks, has been corrected accordingly.

Fig. 4 and Fig 7. Please state in the figure captions what the error bars represent.

The error bars represent one standard deviation of diel mean values. This is now specified in the figure captions of the revised manuscript (Fig. 4 and 7).

References

Sörgel, M., Trebs, I., Serafimovich, A., Moravek, A., Held, A., and Zetzsch, C.: Simultaneous HONO measurements in and above a forest canopy: influence of turbulent exchange on mixing ratio differences, Atmos. Chem. Phys., 11, 841-855, 2011(b)

Alicke, B., Platt, U., Stutz, J.: Impact of nitrous acid photolysis on the total hydroxyl radical budget during the limitation of oxidant production/pianura padana produzione di ozono study in Milan. Journal of Geophysical Research 107 (D22), 8196, 2002.

Alicke, B., Geyer, A., Hofzumahaus, A., Holland, F., Konrad, S., Paetz, H.W., Schaefer, J., Stutz, J., Volz-Thomas, A., Platt, U.: OH formation by HONO photolysis during the BERLIOZ experiment. Journal of Geophysical Research 108 (D4), 8247, 2003.

Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., and Troe, J.: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume I - gas phase reactions of O-x, HOx, NOx and SOx species, Atmospheric Chemistry and Physics, 4, 1461-1738, 2004.

Su, H., Cheng, Y. F., Cheng, P., Zhang, Y. H., Dong, S., Zeng, L. M., Wang, X., Slanina, J., Shao, M., and Wiedensohler, A.: Observation of nighttime nitrous acid (HONO) formation at a non-urban site during PRIDE-PRD2004 in China, Atmospheric Environment, 42, 6219-6232, 2008(b).

Spataro, F., Ianniello, A., Esposito, G., Allegrini, I., Zhu, T., and Hu, M.: Occurrence of atmospheric nitrous acid in the urban area of Beijing (China), The Science of the total environment, 447, 210-224, 2013.

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 $1x10^6$ 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.

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

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.

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

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."

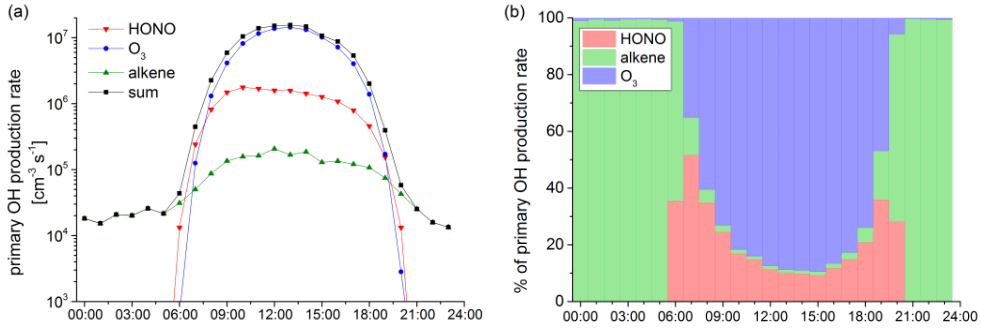
Specific Comment:

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.

References:

Mamtimin, B., Meixner, F. X., Behrendt, T., Badawy, M., and Wagner, T.: The contribution of soil biogenic NO and HONO emissions from a managed hyperarid ecosystem to the regional NOx emissions during growing season, Atmos. Chem. Phys., 16, 10175-10194, 2016.

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Oikawa, P. Y., Ge, C., Wang, J., Eberwein, J. R., Liang, L. L., Allsman, L. A., Grantz, D. A., and Jenerette, G. D.: Unusually high soil nitrogen oxide emissions influence air quality in a high-temperature agricultural region, Nat. Commun., 6, 2015.

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Daytime formation of nitrous acid at a coastal remote site in Cyprus indicating a common ground source of atmospheric HONO and NO

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Abstract. Characterization of daytime sources of nitrous acid (HONO) is crucial to understand atmospheric oxidation and radical cycling in the planetary boundary layer. HONO and numerous other atmospheric trace constituents were measured on the Mediterranean island of Cyprus during the CYPHEX campaign (CYPHEX = CYprus PHotochemical EXperiment) in summer 2014. Average volume mixing ratios of HONO were 35 pptv (±25 pptv) with a HONO/NO_x ratio of 0.33, which was considerably higher than reported for most other rural and urban regions. Diel profiles of HONO showed peak values in the late morning (60±28 pptv around 09:00 local time), and persistently high mixing ratios during daytime (45±18 pptv) indicating that the photolytic loss of HONO is compensated by a strong daytime source. Budget analyses revealed unidentified sources producing up to 3.4 x 10^6 molecules cm^{-3} s^{-1} of HONO and up to 2.0 x 10^7 molecules cm^{-3} s^{-1} NO. Under humid conditions (RH >70%), the source strengths of HONO and NO exhibited a close linear correlation (R^2=0.7~~8~~2), suggesting a common source that may be attributable to emissions from microbial communities on soil surfaces.

1 Introduction

Nitrous acid (HONO) is an important component of the nitrogen cycle being widely spread in the environment. Either in its protonated form (HONO or HNO_2) or as nitrite ions (NO_2^-) it can be found in the gas phase, on aerosol-particles, in clouds and dew droplets but also in soil, sea-water and sediments (Foster et al., 1990; Rubio et al., 2002; Acker et al., 2005 and 2008; Bianchi et al., 1997). It plays a key role in the oxidizing capacity of the atmosphere, as it is an important precursor of the OH radical, which initiates most atmospheric oxidations. OH radicals react with pollutants in the atmosphere to form mostly less toxic compounds (e.g. CO + OH → CO_2 + H_2O; Levy, 1971). Volatile organic compounds (VOCs) react with OH contributing to formation of secondary aerosols (SOA), which

can serve as cloud condensation nuclei CCN (Arey et al., 1990; Duplissy et al., 2008). Furthermore OH oxidizes SO_2 to H_2SO_4, which condense subsequently to form aerosol particles (Zhou et al. 2013). In this way HONO has an indirect effect on the radiative budget and climate. In the first 2-3 hours following sunrise, when OH production from other sources (photolysis of O_3 and formaldehyde) is relatively low, photolysis of HONO can be the major source of OH radicals as HONO concentrations may be high after accumulation during night time (Lammel and Cape, 1996; Czader et al., 2012; Mao et al., 2010). On average up to 30% of the daily OH budget in the boundary layer is provided by HONO photolysis (Alicke et al., 2002; Kleffmann et al., 2005; Ren et al., 2006), but has been reported as high as 56% (Ren et al., 2003) with ambient HONO mixing ratios ranging from several pptv in rural areas up to a few ppb in highly polluted regions (Acker et al., 2006a and 2006b; Costabile et al., 2010; Li et al., 2012; Michoud et al., 2014; Spataro et al., 2013; Su et al. 2008a; Zhou et al., 2002a).

In early studies, atmospheric HONO was assumed to be in at photostationary state during daytime controlled by the gas phase reaction of NO and OH (R1) and two loss reactions which are the photolysis (R2) and the reaction with OH (R3).

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

$$HONO \xrightarrow{hv\,(300-405\ nm)} OH + NO \quad \text{(R2)}$$

$$HONO + OH \rightarrow NO_2 + H_2O \quad \text{(R3)}$$

However, field measurements in remote and rural locations, as well as urban and polluted regions found several times higher daytime HONO concentrations than model predictions, suggesting a large unknown source (Kleffmann et al., 2003 and 2005; Su et al., 2008a; Soergel 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) even after considering direct emission of HONO from combustion sources (Kessler and Platt, 1984; Kurtenbach et al., 2001). Heterogeneous reactions on aerosols have been proposed as an explanation for the missing source. The hydrolysis (R4, Finlayson-Pitts et al., 2003) and redox reactions of NO_2 have been intensively investigated on different kinds of surfaces such as fresh soot, aged or organic-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). Minerals like SiO_2, $CaCO_3$, CaO, Al_2O_3, and Fe_2O_3 showed a catalytic effect on the hydrolysis of NO_2 (Kinugawa et al., 2011; Liu et al., 2015; Wang et al., 2003; Yabushita et al., 2009). Different kind of surfaces (humic acid and other organic compounds, titanium dioxide, soot) can be photochemically activated which leads to enhanced NO_2 uptake and HONO production (R5,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). The photolysis of particulate nitric acid (HNO_3), nitrate (NO_3^-) and nitro-phenols (R-NO_2) lead to HONO formation as well (Baergen and Donaldson, 2013; Bejan et al., 2006; Ramazan et al., 2004; Scharko et al., 2014; Zhou et al., 2003; Zhou et al., 2011). But these reactions cannot account for the HONO levels observed during daytime (Elshorbany et al., 2012).

$$2\,NO_2 + H_2O \rightarrow HONO + HNO_3 \quad \text{(R4)}$$

$$surface \xrightarrow{hv} e^- \xrightarrow{NO_2} NO_2^- \xrightarrow{H_2O} HONO + OH^- \quad \text{(R5)}$$

On the other hand, soil nitrite, either biogenic or non-biogenic, has been suggested as an effective source of HONO (Su et al., 2011; Oswald et al., 2013; Mamtimin et al., 2016). Depending on soil properties such as pH and water content and according to Henry´s law HONO can be released (Donaldson et al., 2014b; Su et al., 2011). This is consistent with field flux measurements showing HONO emission from the ground rather than deposition as is the case for HNO_3 (Harrison and Kitto, 1994; Kleffmann et al., 2003; Ren et al., 2011; Stutz et al., 2002; VandenBoer et al., 2013; Villena et al., 2011; ~~Wong et al., 2012 and 2013;~~ Zhou et al., 2011). In a recent study, Weber et al. (2015) measured large HONO- and NO-emissions from dryland soils with microbial surface communities (so-called biological soil crusts). 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.

Several field studies also show a correlation of the unknown HONO source with solar radiation or the photolysis frequency of NO_2 J_{NO2} (Su et al., 2008a; S~~ö~~oergel et al., 2011a; Wong et al., 2012; Costabile et al., 2010; Michoud et al., 2014; Oswald et al., 2015; Lee et al., 2016). This correlation can be explained either by the aforementioned photosensitized reactions or by temperature-dependent soil-atmosphere exchange (Su et al., 2011). According to Su et al. (2011), the release of HONO from soil surfaces is controlled by both the soil (biogenic and chemical) production of nitrite and the gas-liquid phase equilibrium. The solubility is strongly temperature-dependent, resulting in a higher HONO emission during noon time and high radiation J_{NO2} periods, and lower HONO emissions or even HONO deposition during the nighttime as further confirmed by VandenBoer et al. (2015). This temperature dependence not only exists for equilibrium over soil solution but also exists for adsorption/desorption equilibrium over dry and humid soil surfaces (Li et al., 2016).

In this study we measured HONO and a suite of other atmospherically relevant trace gases in a coastal area on the Mediterranean Island Cyprus in summer 2014. Due to low local anthropogenic impact and low NOx levels in aged air masses, but high solar radiation, this is an ideal site to investigate possible HONO sources and to gain a better understanding of HONO chemistry.

2 Instrumentation

HONO was measured with a commercial Long Path Absorption Photometry instrument (effective light path 1.5 m, LOPAP, Quma, Wuppertal, Germany). LOPAP has a collecting efficiency of >99% for HONO and a detection limit of 4 pptv at a time resolution of 30s. To avoid potential interferences induced by long inlet lines and heterogeneous formation or loss of HONO on the inlet walls, respectively (Kleffmann et al., 1998; Zhou et al., 2002b; Su et al., 2008b), HONO was collected by a sampling unit installed directly in the outdoor atmosphere, i.e., placed on a mast at a height of 5.8 meters above ground installed at the edge of a laboratory container. Furthermore, the LOPAP has two stripping coils placed in series to reduce known interfering signals (Heland et al., 2001). In the first stripping coil HONO is quantitatively collected. Due to the acidic stripping solution interfering species are collected less

efficiently but in both channels. The true concentration of HONO is obtained by subtracting the inferences quantified in the second channel (in this study average 1 pptv, at most 5 pptv) from the total signal obtained from the first channel. For a more detailed description of LOPAP, see Heland et al. (2001). This correction of chemical interferences ascertained excellent agreement with the (absolute) DOAS measurements, both in a smog chamber and under urban atmospheric conditions (Kleffmann et al., 2006). A possible interference from peroxynitric acid (HNO_4) has been proposed (Liao et al., 2006; Kerbrat et al., 2012; Legrand et al., 2014), but this will be insignificant at the high temperatures during CYPHEX, at which HNO_4 is unstable. The stripping coils are temperature controlled by a water-based thermostat and the whole external sampling unit is shielded from sunlight by a small plastic housing. The reagents were all high purity grade chemicals, i.e., hydrochloric acid (37%, for analysis; Merck), sulfanilamide (for analysis, >99%; AppliChem) and N-(1-naphthyl)-ethylenediamine dihydrochloride (for analysis, >98%; AppliChem). For calibration Titrisol® 1000 mg NO_2^- ($NaNO_2$ in H_2O; Merck) was diluted to 0.0015 and 0.005 mg/L NO_2^-. For preparation all solutions and for cleaning of the absorption tubes 18 MΩ H_2O was used. The accuracy of the HONO measurements was 10%, based on the uncertainties of liquid and gas flow, concentration of calibration standard and regression of calibration.

NO and NO_2 measurements were made with a modified commercial chemiluminescence Detector (CLD 790 SR) originally manufactured by ECO Physics (Duernten, Switzerland). The two-channel CLD based on the chemiluminescence of the reaction between NO and O_3 was used for measurements of NO and NO_2. NO_2 was measured as NO using a photolytic converter from Droplet Measurement Technologies, Boulder USA. In current study, data were obtained at a time resolution of 5 seconds. The CLD detection limits (determined by continuously measuring zero air at measuring site) for NO and NO_2 measurements were 5 pptv and 20 pptv, respectively for an integration period of 5 s. O_3 was measured with a standard UV photometric detector (Model 49, Thermo Environmental Instruments Inc.) with a detection limit of 1 ppb. Data are reported for an integration period of 60 s. The total uncertainties (2σ) for the measurements of NO, NO_2 and O_3 were determined to be 20%, 30% and 5%, respectively, based on the reproducibility of in-field background measurements, calibrations, the uncertainties of the standards and the conversion efficiency of the photolytic converter (Li et al., 2015).

OH and HO_2 radicals were measured using the HydrOxyl Radical measurement Unit based on fluorescence Spectroscopy (HORUS) setup developed at the Max Planck Institute for Chemistry (Mainz, Germany). HORUS is based on laser induced fluorescence- fluorescence assay by gas expansion (LIF-FAGE) technique, wherein OH radicals are selectively excited at low pressure by pulsed UV light at around 308 nm, and the resulting fluorescence of OH is detected using gated microchannel plate (MCP) detectors (Martinez et al., 2010; Hens et al., 2014). The HORUS instrument had an inlet pre-injector (IPI) (Novelli at al. 2014) which allows the periodic addition of propane to scavenge the atmospheric OH radicals. This procedure allows the removal of potential interference species. HO_2 is estimated by converting atmospheric HO_2 into OH using NO, and detecting the additional OH formed. The instrument is calibrated by measuring signals from known amounts of OH and HO_2 generated by photolysis of water vapor in humidified zero air. The accuracy (2 sigma) of the OH measurements was 29% and the precision (1 sigma) was 4.8×10^5 molecules cm^{-3}.

Photolysis frequencies were determined using a spectroradiometer (Metcon GmbH) with a single monochromator and 512 pixel CCD-array as detector (275-640 nm). The thermostatted monochromator/detector unit was attached via a 10 m optical fiber to a 2-Π integrating hemispheric quartz dome. The spectroradiometer was calibrated prior to the campaign using a 1000 W NIST traceable irradiance standard. J-values were calculated using molecular parameters recommended by the IUPAC and NASA evaluation panels (Sander et al., 2011; IUPAC, 2015). The J-value for HONO was not corrected for upwelling UV radiation and is estimated to have an uncertainty of ~10 % (Bohn et al., 2008).

Aerosol measurements were also performed during the campaign. In this study particulate nitrate and aerosol surface data were used. These were detected by high resolution – time of flight – aerosol mass spectrometer (HR-ToF-AMS, Aerodyne Research Inc., Billerica, MA USA) and scanning mobility particle sizer (SMPS 3936, TSI, Shoreview, MN USA) and aerodynamic particle sizer (APS 3321, TSI), respectively. The mobility and aerodynamic based size distributions were combined based on the algorithm proposed by Khlystov et al. (2004).

The volatile organic compounds (VOC) including α-pinene, β-pinene, isoprene, Δ3-carene, limonene and DMS (dimethyl sulfide) were detected by a commercial Gas Chromatography-Mass Spectrometry (GC-MS) system (MSD 5973; Agilent Technologies GmbH) coupled with an air sampler and a thermal desorber unit (Markes International GmbH). The VOCs were trapped at 30^{o}C on a low-dead-volume quartz cold trap (U-T15ATA; Markes International GmbH) filled with two bed sorbent (Tenax TA and Carbograph I). The cold trap was heated to 320^{o}C and the sample was transferred to a 30m GC column (DB-624, 0.25mm I.D., 1.4µm film; J&W Scientific). The temperature of the GC oven was programmed to be stable at 40^{o}C for 5mins and then rising with a rate of 5^{o}C/min up to 140^{o}C. Following, the rate was increased to 40^{o}C/min up to 230^{o}C where it was stabilized for 3min. Each sample was taken every 45mins and calibrations, using a commercial gas standard mixture (National Physical Laboratory, UK), were performed every 8-12 samples.

~~Formaldehyde (HCHO) was measured with a commercial analyzer based on the Hantzsch reaction. The product of the reaction of HCHO with acetyl acetone and ammonia absorbs light at 410 nm and fluoresces at 510 nm which is detected (AL4011, Aerolaser GmbH, Garmisch-Partenkirchen, Germany).~~

Carbon monoxide was measured by infrared absorption spectroscopy using a room temperature quantum cascade laser at a time resolution of 1 s. Data are reported as 60 s averages with a total uncertainty of ~10% mainly determined by the uncertainty of the used NIST standard (Li et al., 2015).

Meteorological parameters (temperature, relative humidity, wind speed and wind direction, pressure, solar radiation, precipitation) were detected by the weather station Vantage Pro2 from DAVIS.

Besides GC-MS all other operating instruments had time resolutions between 20 s and 5 min. For most analyses in this study the data were averaged to 10 min. When GC-MS data were included in the evaluation 1 hour averaged data were used.

3 Site description

Cyprus is a 9251 km² island in the South-East Mediterranean Sea (fig. 1). The measuring site was located on a military compound in Ineia, Cyprus (N 34.9638, E 32.3778), about 600 m above sea level and approximately 5.5 - 8

km from the coast line (in the main wind direction W-SW). The field site is characterized by light vegetation cover, mainly comprising small shrubs like *Pistacia lentiscus, Sacopoterium spinosum,* and *Nerium oleander,* herbs like *Inula viscosa* and *Foeniculum vulgare* and few typical Mediterranean trees like *Olea europaea, Pinus* sp., *and Ceratonia siliqua.*. The area within a radius of about 15 km around the station is only weakly populated. Paphos (88,266 citizens) is located 20 km south of the field site, Limassol (235,000), Nicosia (325,756) and Larnaca (143,367) are 70, 90 and 110 km in the E-SE, respectively (population data according to statistical service of the republic of Cyprus, www.cystat.gov.cy, census of population Oct 2011). During the campaign (07.07. - 04.08.2014), clear sky conditions prevailed and occasionally clouds skimmed the site. No rain was observed, but the elevated field site was impacted by fog during nighttime and early morning due to adiabatic cooling of ascending marine humid air masses. Temperature ranged from 18 to 28°C. Within the main local wind direction of SW (fig. 2A) there was no direct anthropogenic influence resulting in clean humid air from the sea. Analysis of 48-hours back trajectories showed mainly two source regions of air mass origin (fig. 2B). Approximately half (46%) of the campaign the air masses came from the West of Cyprus spending most of their time over the Mediterranean Sea prior to arriving at the site. During the remaining half of the campaign air masses originated from the North of Cyprus, from East European countries (Turkey, Bulgaria, Rumania, Ukraine and Russia). Westerly air masses have been shown to exhibit lower concentration of gaseous and aerosol pollutants than the predominant northerly air masses that typically reach the site (Kleanthous et al., 2014). They spent more time over continental terrestrial surface and were likely to be additionally affected by biomass burning events detected in East Europe within the measurement periods (FIRMS, MODIS, web fire mapper, fig. S1). Previous back trajectory studies in the eastern Mediterranean support this assumption (Kleanthous et al., 2014; Pikridas et al., 2010).

Most of the time the advected air mass was loaded with high humidity as a result of sea breeze circulation. Two periods of about 4 days with lower relative humidity occurred. These two situations will be contrasted below.

4 Results

The concentrations of HONO and other atmospheric trace gases as well as meteorological conditions observed on Cyprus from 7th July 2014 to 3rd August 2014 are shown in fig. 3. In general, low trace gas mixing ratios were indicative of clean marine atmospheric boundary conditions, as pollutants are oxidized by OH during the relatively long air transport time over the Mediterranean sea (more than 30 h), and without significant impact of direct anthropogenic emissions.

Ambient HONO mixing ratios ranged from below detection limit (< 4 pptv) to above 300 pptv. Daily average HONO was 35 pptv (± 25 pptv; 1σ standard deviation, following alike). The daily average NO_2 and NO mixing ratios were 140 ± 115 and 20 ± 35 pptv respectively, but showed intermittent peaks up to 50 ppbv when sampling air was streamed from the diesel generator used to power the station, from the access route or the parking lot by local winds (easterly, fig S2). These incidents, which account for 4% of the campaign time, were classified as local air pollution events and were omitted from analysis. Mean O_3 and CO mixing ratios were 72 ± 12 ppb and 98 ± 11 ppbv respectively. OH radicals ranged from below detection limit ($1x10^5$ molecules cm^{-3}) during nighttime to $8x10^6$ molecules cm^{-3} during daytime (see fig. S3). Daytime HO_2/OH ratio ranged from 100 to 150. The mixing ratios of

NO_2, O_3 and CO varied in unison, and were significantly ($p<0.05$) higher during periods when air masses originated from East Europe (brownish bar in fig. 3a lower panel), indicative of air pollution and shorter transport times compared to western Europe (NO_2: Northerly: 144 ± 130 pptv, westerly: 127 ± 106 pptv; O_3: Northerly: 74 ± 11 ppbv, westerly: 66 ± 12 ppbv; CO: Northerly: 101 ± 9 ppbv, westerly: 90 ± 10 ppbv). In contrast, NO and HONO mixing ratios were slightly higher when air masses came from Western Europe and over the sea (NO: Northerly: 17 ± 35 pptv, westerly: 20 ± 44 pptv; HONO: Northerly: 32 ± 26 pptv, westerly: 38 ± 22 pptv).

Besides two different air mass origins, two periods with different behaviour of relative humidity were identified illustrated by blue and yellow boxes in fig. 3(a and b). In both periods we found northerly and westerly air mass origins. The diel profiles of trace gas mixing ratios and meteorological variables of the humid period (blue box) are shown in Fig. 4a, the ones of the dry period (yellow box) in Fig 4b. During the drier period HONO concentrations are stable and low (6 pptv) during night, while mean nighttime HONO mixing ratios during the humid period (fig. 4a) showed an expected slow increase of about 20 pptv (from 20 to 40 pptv), as anticipated from heterogeneous production and accumulation within a nocturnal boundary layer characterized by a stable stratification and low wind speed (Acker et al., 2005; Su et al., 2008b; Li et al., 2012). During both periods, but more pronounced in the drier period, HONO rapidly increased by a factor of 2 within two hours after sunrise and then slowly decreased until sunset. Similar profiles were also observed for other trace gases like isoprene or DMS which are transported in upslope winds. Strong HONO morning peaks and high daytime mixing ratios suggest a strong daytime source, compensating the short atmospheric lifetime (15 min) caused by fast photolysis.

Mean NO mixing ratios were close to the detection limit (~~52~~ pptv) during night and increased after sunrise (06:00 local time LT) to mean values of 60 pptv (peak 150 pptv) at 09:00 LT, prior to declining for the rest of the day until sunset (20:00 LT). 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 (~~Hosaynali~~ Beygi et al., 2011). The diel profiles of NO mixing ratios followed closely those of HONO mixing ratios. This similarity and their dependency on relative humidity are suggestive of a common source for both reactive nitrogen species.

NO_2 mixing ratios were somewhat lower during nighttime, but in general the diel variability remained in a narrow range between 100 and 200 pptv. Likewise, the diel courses of O_3 and CO mixing ratios revealed relatively low day/night variability in a range of 65-75 and 90-100 ppb, respectively.

5 Discussion

Low NO_x conditions at this remote field site in photochemically aged marine air were found to be an ideal prerequisite to trace yet un-defined local HONO sources. On Cyprus, diel profiles of HONO showed peak values in the late morning and persistently high mixing ratios during daytime, as has been reported for some other remote regions (Acker et al., 2006a; Zhou et al., 2007; Huang et al., 2002). This is not the case for rural and urban sites, where atmospheric HONO mixing ratios are normally observed to continuously build up during nighttime presumably due to heterogeneous reactions involving NO_x and decline in the morning due to strong photodissociation (e.g., Elshorbany et al., 2012 and references therein).

The diel HONO/NO_x ratio (fig. 4a+b, third panel) shows consistently high values during the humid period (fig. 4a) and significant diel variation for the dry case (fig. 4b) with higher values during day. The ratio (average 0.33 and peak values greater than 2) is higher than that reported for most other regions, suggesting a strong impact of local HONO sources. Elshorbany et al. (2012) investigated data from 15 different urban and rural field measurement campaigns around the globe, and came up with a robust representative mean atmospheric HONO/NOx ratio as low as 0.02. However, high values were observed at remote mountain sites, with mean values of 0.23 (up to ≈0.5 in the late morning; Zhou et al., 2007) or 0.2–0.4 at remote arctic/polar sites (Li, 1994; Zhou et al., 2001; Beine et al., 2001; Jacobi et al., 2004; Amoroso et al., 2010). Legrand et al. (2014) observed HONO/NO_x ratios between 0.27 and 0.93 during experiments with irradiated Antarctic snow depending on radiation wavelength, temperature and nitrate content. Elevated HONO/NO_x ratios at low NO_x levels show the importance of HONO formation mechanisms other than heterogeneous NO_x reactions.

5.1 Nighttime HONO accumulation

Between 18:30 – 7:30 LT HONO has an atmospheric lifetime of more than 45 min and [OH] is low, just about $1x10^5$ molecules cm^{-3}, so that the calculation of HONO at photostationary state $[HONO]_{pss}$ (R1-R3) at night is not appropriate. Instead, nighttime HONO concentrations can be estimated due to heterogeneous reaction of NO_2 described in Eq. (1) (Alicke et al., 2002+2003; Su et al., 2008b; Soergel et al., 2011b). Three studies in different environments from a rural forest region in East Germany (Sörgel et al., 2011b) and a non-urban site in the Pearl River delta, China (Su et al., 2008b) to an urban, polluted site in Beijing (Spataro et al., 2013) found a conversion rate of about 1.6% h^{-1} (1.1-1.8 % h^{-1}).

$$[HONO]_{het} = [HONO]_{evening} + 0.016\ h^{-1}[NO_2]\ \Delta t, \qquad \text{(Eq. 1)}$$

$[HONO]_{het}$ denotes the accumulation of HONO by heterogeneous conversion of NO_2, $[HONO]_{evening}$ the measured HONO ~~mixing ratio~~concentration at ~~18~~20:30 LT, $[NO_2]$ the measured average NO_2 ~~mixing ratio~~concentration between ~~18~~20:30 and 7:30 LT, Δt time span in hours.

Measured and calculated HONO mixing ratios are compared in figure 4 (upper panel). During the humid period, during night the estimated (according Eq. (1), fig. 4a upper panel, grey line) and observed HONO mixing ratios are in good agreement (R^2 = 0.9). During the drier period the observed HONO mixing ratios were lower than the ones calculated with a NO_2 conversion rate of 1.6% h^{-1}. ~~But Kleffmann et al., 2003 found a smaller conversion rate of 6 x 10^{-7} s^{-1} (0.22% h^{-1}) for rural forested land in Germany which matches better to the observed nighttime HONO concentration during drier period (fig. 4b upper panel, dark grey line).~~ Here the approach for the nighttime conversion frequency by e.g. Alicke et al., 2002+2003, Su et al., 2008b or Soergel et al., 2011b (rate = $\frac{HONO_{t2}-HONO_{t1}}{\Delta t * \overline{NO_2}}$) was used. The 7 days average conversion rate for the dry nights was 0.36% h^{-1} (fig. 4b, upper panel, black line), comparable to results of Kleffmann et al. (2003) reporting a conversion rate of $6x10^{-7}$ s^{-1} (0.22% h^{-1}) for rural forested land in Germany.

As already mentioned above, it is apparent that under low RH conditions during night, HONO mixing ratios were much lower than under humid conditions, and HONO morning peaks were most pronounced (compare Fig. 4a and 4b: humid/dry). Both HONO (Donaldson et al., 2014a) and NO_2 (Wang et al., 2012; Liu et al., 2015) uptake

coefficients have recently been reported to be much stronger for dry soil, or at low RH, respectively, which is in line with HONO on Cyprus being close to the detection limit in nights with low relative humidity. On the other hand, it has been shown on glass and on soil proxies that the yield of HONO formation from NO_2 on surfaces is low under dry conditions, but sharply increases at RH >30% (Liu et al., 2015) or >60% (Finlayson-Pitts et al., 2003). On Cyprus the strong morning HONO peaks after dry nights were accompanied by an increase in relative humidity from 40 to 80%. Deposited and accumulated NO_2 on dry soil surfaces could be released as HONO at high rates under elevated RH conditions. In contrast, in a humid regime HONO mixing ratios were continuously high during nighttime and showed less pronounced morning peaks, suggesting lower nighttime deposition of NO_2 and lower HONO emissions in the morning, respectively.

As morning HONO peak mixing ratios were most pronounced after dry nights on Cyprus, our observations are to some extent contradictory to earlier results that have proposed that dew formation on the ground surface may be responsible for HONO nighttime accumulation in the aqueous phase, followed by release from this reservoir after dew evaporation the next morning (Zhou et al., 2002a, Rubio et al., 2002, He et al., 2006). We cannot rule out that the latter could have contributed to nighttime accumulation of HONO during humid conditions, as we had no means to measure dew formation at the site, and high daytime HONO mixing ratios were observed under all humidity regimes. However, kinetic models of competitive adsorption of trace gases and water onto particle surfaces predict exchange behavior explicitly distinct from the liquid phase (Donaldson et al., 2014a). The nitrogen composition in thin water films (few water molecular monolayers) is complex, including HONO, NO, HNO_3, water–nitric acid complexes, NO_2^+ and N_2O_4 (Finlayson-Pitts et al., 2003). With only small amounts of surface-bound water, nitric acid is largely undissociated HNO_3 and is assumed to be stabilized upon formation of the HNO_3–H_2O complexes (hydrates), which have unique reactivity compared to nitric acid water aqueous solutions, where it is dissociated H^+ and NO_3^- ions (Finlayson-Pitts et al., 2003). Likewise, HONO formation rates in surface bound water are about four orders of magnitude larger than expected for the aqueous phase reaction (Pitts et al., 1984).

Diel HONO profiles very similar to those on Cyprus with a late morning maximum and late afternoon/early evening minimum have been observed at the Meteorological Observatory Hohenpeissenberg, a mountain-top site in Germany (Acker et al., 2006a) and by Zhou et al. (2007) at the summit of Whiteface Mountain in New York State. For the latter study, formation of dew could be ruled out as relative humidity was mostly well below saturation. Zhou et al. (2007) argued that the high HONO mixing ratios during morning and late morning can be explained by mountain up-slope flow of polluted air from the cities at the foot of the mountain that results from ground surface heating. On Cyprus the sea breeze, driven by the growing difference between sea and soil surface temperature, brings air to the site which interacted with the soil surface and vegetation and is loaded by respective trace gas emissions. This is endorsed by the simultaneous increase of DMS and isoprene, markers for transportation of marine air and emission by vegetation. In the late afternoon, when the surface cools, down-welling air from aloft would dominate, being less influenced by ground surface processes. Zhou et al. (2007) could show that noontime HONO mixing ratios and average NO_y during the previous 24-hour period were strongly correlated, much better than instantaneous $HONO/NO_y$ or $HONO/NO_x$, which is in line with N-accumulation on soil surfaces as discussed above.

5.2 Daytime HONO budget

During daytime (7:30 to 18:00 LT, with HONO lifetime being between 10 and ~~less than~~ 30 min), $[HONO]_{PSS}$, the photostationary HONO ~~mixing ratios~~concentration resulting from gas phase chemistry can be calculated according to Eq. (2) (Kleffmann et al., 2005):

$$[HONO]_{PSS} = \frac{k_1[OH][NO]}{k_2[OH]+J_{HONO}} \quad \text{(Eq.2)}$$

where k_1 and k_2 are the temperature dependent rate constants for the gas phase HONO formation from NO and OH and the loss of HONO by reaction of HONO and OH, respectively (Atkinson et al., 2004; e.g. at 23.0°C a typical temperature during this study $k_1 \approx 1.36 \times 10^{-11}$ $cm^3 s^{-1}$; $k_2 \approx 6.01 \times 10^{-12}$ $cm^3 s^{-1}$). J_{HONO} is the photolysis frequency of HONO, which was measured with a spectroradiometer. [NO] is the observed NO ~~mixing ratio~~concentration. Since OH data were available only on a few days, diel variations of [OH] were averaged (see fig. S3).

As has been previously established by many other studies (Su et al., 2008~~b~~a; Michoud et al., 2014; Soergel et al., 2011a), homogeneous gas-phase chemistry alone fails to reflect observed HONO mixing ratios. Observed daytime values were up to 30 times higher than calculated based on PSS, indicating strong additional local daytime sources of HONO. 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.

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

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. $\Delta[HONO]/\Delta t$ 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~~The strength of these sources (S_{HONO}) can be calculated by following equation:~~

~~$$S_{HONO} = ([HONO]_{measured} - [HONO]_{PSS}) \cdot (k_2[OH] + J_{HONO}) \quad \text{(Eq. 3)}$$~~

In the late morning (around 10:00 LT) the unknown source was at its maximum with peak production rates of up to 3.4×10^6 molecules cm^{-3} s^{-1}, and a daytime average of about 1.3×10^6 cm^{-3} s^{-1}, which is in good agreement with other studies at rural sites like a mountain site at Hohenpeissenberg ($(3\pm1) \times 10^6$ cm^{-3} s^{-1}, at $NO_x \approx 2$ ppbv, Acker et al., 2006a), a deciduous forest site in Jülich (3.45×10^6 molecules cm^{-3} s^{-1}, at NO ≈ 250 pptv, Kleffmann et al., 2005) and a pine forest site in South-West Spain 0.74×10^6 molecules cm^{-3} s^{-1}, at $NO_x \approx 1.5$ ppbv, S~~ö~~oergel et al., 2011a) but

smaller than at urban sites in Houston (4-6x10^6 cm^{-3} s^{-1}, at NO_x ≈ 6ppbv, Wong et al., 2012), Beijing (7x10^6 cm^{-3} s^{-1}, at NO_x ≈15 ppbv, Yang et al., 2014) and South China (5.25 ± 3.75x10^6 cm^{-3} s^{-1}, at NO_x ≈ 20 ppbv, Li et al., 2012; or 1-4x10^7 cm^{-3} s^{-1}, at NO_x ≈ 35 ppbv, Su et al., 2008a).

The contributions of gas phase reactions and the heterogeneous reaction of NO_2 (conversion rate (a) 1.6% h^{-1} and (b) 0.36% h^{-1}) to the HONO budget are illustrated in fig. 5, exemplary. For both periods the contributions are quiet similar just the absolute values are different. To compensate the strong loss via photolysis a comparable strong unknown source is necessary as the heterogeneous NO_2 conversion or the gasphase reaction of OH and NO are insignificant.

In polluted regions with moderate to high NO_x concentrations, HONO sources have often been linked with $[NO_2]$ or $[NO_x]$ (Acker et al., 2005, Li et al., 2012, Levy et al., 2014, Soeörgel et al., 2011a, Wentzel et al., 2010). Under the prevailing low NO_x conditions during CYPHEX (<250 pptv), correlation analysis (see table 1) of S_{HONO} with $[NO_2]$ (R^2 = 0.4450) and $[NO_2]$*RH (R^2 = 0.4651) indicate no significant impact of instantaneous heterogeneous formation of HONO from NO_2. Better correlations of S_{HONO} with J_{NO2} (R^2 = 0.674) and J_{NO2}*$[NO_2]$ (R^2 = 0.842) indicate a photo-induced conversion of NO_2 to HONO as already suggested by George et al. (2005) or Stemmler et al. (2006, 2007). 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. Other light dependent reactions such as the photolysis of nitrate might additionally contribute to high daytime HONO. It is unlikely that aerosol surfaces played an important role in heterogeneous conversion of NO_2 as the mean observed aerosol surface concentration was only about 300 μm^2 cm^{-3}. Based on a formula for photo enhanced conversion of NO_2 on humic acid aerosols which was derived by Stemmler et al. (2007) a HONO formation rate of only 5.1x10^2 molecules cm^{-3} s^{-1} can be estimated. Likewise, Söoergel et al. (2015) showed that HONO fluxes from light-activated reactions of NO_2 on humic acid surfaces at low NO_2 levels (< 1 ppb and thus comparable to concentrations observed in this study) saturated at around 0.0125 nmol m^{-2} s^{-1}. Therefore heterogeneous aerosol surface reactions can be neglected as HONO sources at the prevailing low NO_x levels.

Likewise, the nitrate concentrations of highly acidic marine aerosols particulate matter as measured by HR-ToF-AMS (PM1 fraction, mean 0.075 µg m^{-3}) were too low to account for significant photolytic HONO production (1.7x10^2 molecules cm^{-3} s^{-1} or 0.01% of S_{HONO}) calculated by Eq. (4):

$$S_{photo\_NO_3^-} = [\overline{NO_3^-}] \cdot J_{NO_3^-} \quad \text{(Eq. 4)}$$

with S_{photo_NO3-} the source strength of HONO by photolysis of nitrate, $[\overline{NO_3^-}]$ the mean particulate nitrate concentration and $J_{NO_3^-}$ the photolysis frequency of nitrate (aqueous) at noon (3-x-10^{-7} s^{-1}, Jankowski et al., 1999).

Recently an enhancement of the photolysis frequency of particulate nitrate relative to gaseous or aqueous nitrate was found (Ye et al., 2016). But even with this enhanced rate of 2x10^{-4} s^{-1} not more than 1.1x10^5 molecules cm^{-3} s^{-1} (8% of S_{HONO}) HONO would be produced.

5.3 Common daytime source of HONO and NO

During CYPHEX, good correlation was found between [HONO] or S_{HONO} and [NO] (R^2 = 0.86 and 0.640, respectively), indicating that both may have a common source. A missing source of NO ~~based on the photostationary state~~ can be calculated as shown in Eq. (5). ~~and (6).~~

~~$$[NO]_{PSS} = \frac{j_{NO_2}[NO_2]+j_{HONO}[HONO]}{k_2[OH]+k_3[HO_2]+k_4[O_3]+k_5[RO_2]}$$ (Eq. 5)~~

$$S_{NO} = ~~([NO]_{measured} - [NO]_{PSS}) \cdot (k_1[OH] + k_2[HO_2] + k_4[O_3] + k_5[RO_2])~~ k_1[OH][NO] + k_3[HO_2][NO] + k_4[O_3][NO] + k_5[RO_2][NO] - J_{NO2}[NO_2] - J_{HONO}[HONO] + \frac{\Delta[NO]}{\Delta t}$$ (Eq. 5~~6~~)

k_3 and k_4 are the temperature dependent rate constants for the reaction of NO with HO_2 and O_3, respectively (Atkinson et al., 2004; at 23°C: $k_3 \approx 8.96 \times 10^{-12}$ $cm^3 s^{-1}$; $k_4 \approx 1.68 \times 10^{-14}$ $cm^3 s^{-1}$), k_5 is the rate constant for the reaction of NO and organic peroxy radicals which was assumed to be the same as for the reaction NO + CH_3O_2 (7.7×10^{-12} $cm^3 s^{-1}$ at 298K, Ren et al., 2010; Sander et al., 2011). Like [OH] also [HO_2] was measured only on a few days and therefore mean diel data were used (fig. S3). Total [RO_2] was estimated to be maximum 1.6*[HO_2] (Ren et al., 2010; Hens et al., 2014). Using a RO_2/HO_2 ratio of 1.2 the absolute values of S_{NO} are reduced by 0.3 to 5.5%. The budget analysis for NO for both humidity regimes is illustrated in fig. S4.

For NO_x, an unexpected deviation from the PSS, or Leighton ratio, respectively, of clean marine boundary layer air has been observed previously, invoking a hitherto unknown NO sink, or pathway for NO to NO_2 oxidation, other than reactions with OH, HO_2, O_3 and organic peroxides (~~Hosaynali~~ Beygi et al., 2011). On Cyprus, two different atmospheric humidity regimes can be differentiated. Under dry conditions (RH < 70%, yellow boxes in fig. 3) and higher NO_x concentrations (>150 pptv) S_{NO} is negative, implying a net NO sink of up to 6.4×10^7 molecules cm^{-3} s^{-1} resembling the above mentioned PSS deviations in remote marine air masses (see fig. 6 and 7). However, during humid conditions (RH > 70, blue boxes in fig. 3) S_{NO} was positive with values of up to 5.1×10^7 molecules cm^{-3} s^{-1}. Due to low and invariant acetonitrile levels, anthropogenic activity and local biomass burning can be excluded as NO source at this specific site. A net NO source during humid conditions is assumed to result from (biogenic) NO emission from soil. As shown in fig. 8, the ~~PSS based~~ S_{HONO} and S_{NO} (time of day-averaged, excluding 3 days as there are transition days 25.7. and 2.8. or the RH changed too quickly 15.7.) were highly correlated (R^2 = 0.728), indicative of both reactive N-compounds being emitted from the same local source. Both HONO and NO have been reported to be released from soil, with a strong dependency on soil water content (Su et al., 2011; Oswald et al., 2013; Mamtimin et al., 2016). The (dry state) soil humidification threshold level for NO emission is reported to be somewhat higher than for HONO (Oswald et al., 2013), which might explain why a net ~~PSS based~~ NO source was preferentially calculated for higher relative humidity conditions, while for HONO ~~the PSS indicated~~ a daytime source under all humidity regimes prevailing during the campaign was found. 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. Analyzing microbial surface

communities from drylands, Weber et al. (2015) observed highly correlated NO-N and HONO-N emissions with Spearman rank correlation coefficients ranging between 0.75 and 0.99. In this study, NO- and HONO-emissions were observed in drying soils with water contents of 20-30% water holding capacity.

Even though we cannot make firm conclusions regarding the exact mechanism of HONO formation, the above mentioned correlation analysis (and table 1) reveal that the instantaneous heterogeneous NO_2 conversion is not a significant HONO source. We propose that HONO is emitted from nitrogen compounds being accumulated on mountain slope soil surfaces produced either biologically by soil microbiota or from previously deposited NO_y. This forms the major daytime HONO source responsible for morning concentration peaks and consistently high daytime mixing ratios at the Cyprus field site. While biological formation is assumed to be more relevant for humid conditions, physical NO_y accumulation can be assumed to be stronger under dry conditions, as uptake coefficients for a variety of trace gases were shown to be significantly higher for dry surfaces, among them NO_2 (Wang et al., 2012, Liu et al., 2015), HONO (Donaldson et al. 2014a) and HCHO (Li et al., 2016). The strongest HONO morning peaks observed after dry nights were accompanied by an increase in relative humidity driven by the sea breeze (fig. 4b), so we consider HONO being released preferentially under favourable humid conditions.

5.4 primary OH production

Many studies showed high contribution of HONO photolysis to the OH budget (up to 30% on daily average; Alicke et al., 2002, Ren et al., 2006). Here the primary OH production rates areis calculated based on the -main OH forming reactions, which are the photolysis of ozoneO_3 and subsequent reaction with water (R6+7), the photolysis of HONO (R2) and HCHO (R8-11) and the reaction of alkenes with ozone (R128).

$$O_3 \xrightarrow{h\nu\ (<340\ nm)} O(^1D) + O_2 \quad \text{(R6)}$$

$$O(^1D) + H_2O \rightarrow 2\,OH \quad \text{(R7)}$$

~~$HCHO \xrightarrow{h\nu\ (<370\ nm)} H + HCO\ (or\ H_2 + CO)$ (R8)~~

~~$H + O_2 \rightarrow HO_2$ (R9)~~

~~$HCO + O_2 \rightarrow CO + HO_2$ (R10)~~

~~$HO_2 + NO\ or\ O_3 \rightarrow OH + NO_2\ or\ 2O_2$ (R11)~~

$$\text{alkene} + O3 \rightarrow OH + \text{other products} \quad \text{(R128)}$$

Reaction rates were taken from Atkinson et al. (2004) and Atkinson (1997). The water pressure over water was calculated according to Murphy and Koop (2005). Reactions of $O(^1D)$ and HO_2 not forming OH are also considered. OH formation yields of the reactions of alkenes with O_3 were taken from Paulson et al. (1999). Photolysis rates (J-values) and concentrations of relevant compounds were as measured on Cyprus. Isoprene, α-pinene, β-pinene, Δ3-carene and limonene (VOC) were taken into account as the most relevant alkenes.

The results of this study are shown in fig. 9. All fourthree production routes show a clear diel profile with higher production rates during daytime. In the night only the reaction of alkenes with O_3 produced significant amounts of OH ($2x10^4$ molecules cm^{-3} s^{-1}). With sunrise the other sources become more relevant. During day Tthe photolysis of HONO and HCHO lead togenerates about similar daytime OH production rates of about 0.8 $1.5x10^6$ molecules OH cm^{-3} s^{-1}, which is about 10 times higher than the ozonolysis of alkenes at that time. The maximum OH production

rate by O_3 photolysis during daytime is about $1.3x10^7$ molecules cm^{-3} s^{-1}. In the morning (6-8 am) and evening hours (7-8 pm) the contribution of HONO photolysis to the ~~total~~primary OH production is in average 3~~7~~0% (see fig. 9b) with peak values of 6~~5~~0%, which is much higher than the contribution of O_3 photolysis at that time. During the rest of the day the contribution of HONO decreases to 12%. ~~The contribution of HCHO is slightly lower.~~ At noon the most dominant OH source is the photolysis of O_3 (more than 80%) while the contribution of the ozonolysis of alkenes is almost negligible (1-2%). A complete and detailed HOx budget analysis with CYPHEX data will be published soon.

6 Conclusion

Nitrous acid was found in low concentrations on the east Mediterranean Island of Cyprus during summer 2014. Daytime concentrations were much higher than during the night and about 30 times higher than would be expected by budget analysis based on photostationary state. The unknown source was calculated to be about $1.9x10^6$ molecules cm^{-3} s^{-1} around noon. Low NO_x concentrations, high $HONO/NO_x$ ratio and low correlation between HONO and NO_2 indicate a local source which is independent from NO_2. Heterogeneous reactions of NO_2 on aerosols play an insignificant role during daytime. Emission from soil, either caused by photolysis of nitrate or gas-soil partitioning of accumulated nitrite/nitrous acid, is supposed to have a higher impact on the HONO concentration during this campaign. Also the NO budget analysis showed a missing source in the humid period, which correlates well with the unknown source of HONO, indicating a common source. The most likely source of HONO and NO is the emission from soil.

Even though the HONO concentration is only in the lower pptv level, it has a high contribution to the primary OH production in the early morning and evening hours.

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Table 1: Linear correlation factors (Pearson correlation, R^2) of HONO and the unknown source S_{HONO} to meteorological factors and different NO_x parameters.

	during the whole campaign		Time of day average	
	HONO	S_{HONO}	HONO	S_{HONO}
T	0.006	0.1325	0.488	0.22714
RH	0.077	0.0045*	0.092	0.1053
Heat flux	0.261	0.300	0.617[c]	0.648585[c]

[a] highly correlated $R^2 > 0.8$

[b] moderate correlated $R^2 > 0.65$

J_{NO2}	0.263	0.39541 4	**0.718**[b]	**0.735672**[b]
NO	0.242	0.206154	**0.857**[a]	0.66400[c]
NO_2	0.052	0.07891	0.620[c]	0.43896
NO_2*RH	0.126	0.11135	0.638[c]	0.505[c]457
NO_2*RH*aerosol surface	0.095	0.11092	0.256	0.56179[c]
NO_2*J	0.191	0.18964	**0.828**[a]	**0.8139**[a]
NO_2*RH*J	0.266	0.25821	**0.850**[a]	**0.8407**[a]
NO_2*RH*J*aerosol surface	0.221	0.20418	**0.806**[a]	**0.8148**[a]
S_{NO}		0.0120		-0.015*0.268

c poorly correlated $R^2 > 0.5$

* anti-correlated

	during the humid period				during the dry period			
			Time of day average				Time of day average	
	HONO	S_{HONO}	HONO	S_{HONO}	HONO	S_{HONO}	HONO	S_{HONO}
T	0.006	0.1216	0.031	0.1123	0.120	0.0163	0.453	-0.00415
RH	0.000	0.08192 *	0.010*	0.12746 *	0.374	0.193227	**0.730**[b]	0.6083[cb]
Heat flux	0.110	0.243	0.184	0.55491[c]	0.502[c]	0.3035	**0.685**[b]	0.59634[c]
J_{NO2}	0.150	0.4657	0.245	**0.69869**[b]	**0.678**[b]	0.32057	**0.829**[a]	**0.65764**[b]
NO	0.168	0.18835	0.418	**0.65076**[b]	0.487	0.32301	**0.730**[b]	0.34029
NO_2	0.066	0.0675	0.300	0.353267	0.037	-0.0023*	0.619[c]	0.1741
NO_2*RH	0.084	0.04853	0.294	0.171245	0.161	0.0210	**0.714**[b]	0.45236[e]
NO_2*RH*aerosol surface	0.047	0.0729	0.111	0.250147	0.241	0.10685	0.557[c]	0.62551[c]
NO_2*J	0.214	0.2691	0.427	**0.910845**[a]	0.358	0.0168	**0.872**[a]	**0.65703**[b]
NO_2*RH*J	0.231	0.24471	0.467	**0.850775**[b]	0.434	0.0685	**0.820**[a]	**0.7703**[b]
NO_2*RH*J*aerosol surface	0.140	0.15260	0.465	**0.78495**[b]	0.414	0.17130	**0.664**[b]	0.67831[c b]
S_{NO}		0.294323		**0.77820**[b]		0.00359 *		-0.0094*

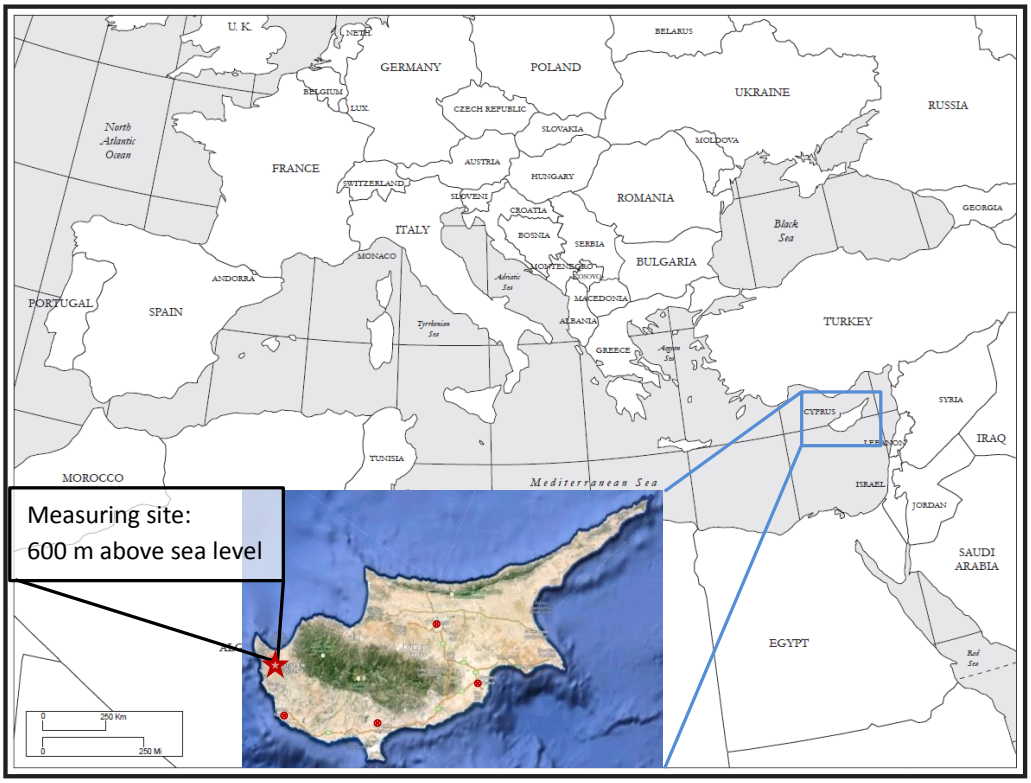


Figure 1: Map of location: the red star shows the location of Ineia and the measuring site. The four red points mark the main cities of Cyprus, Nicosia, Larnaca, Limassol and Paphos (clockwise ordering), map produced by the Cartographic Research Lab University of Alabama, map of Cyprus: google maps.

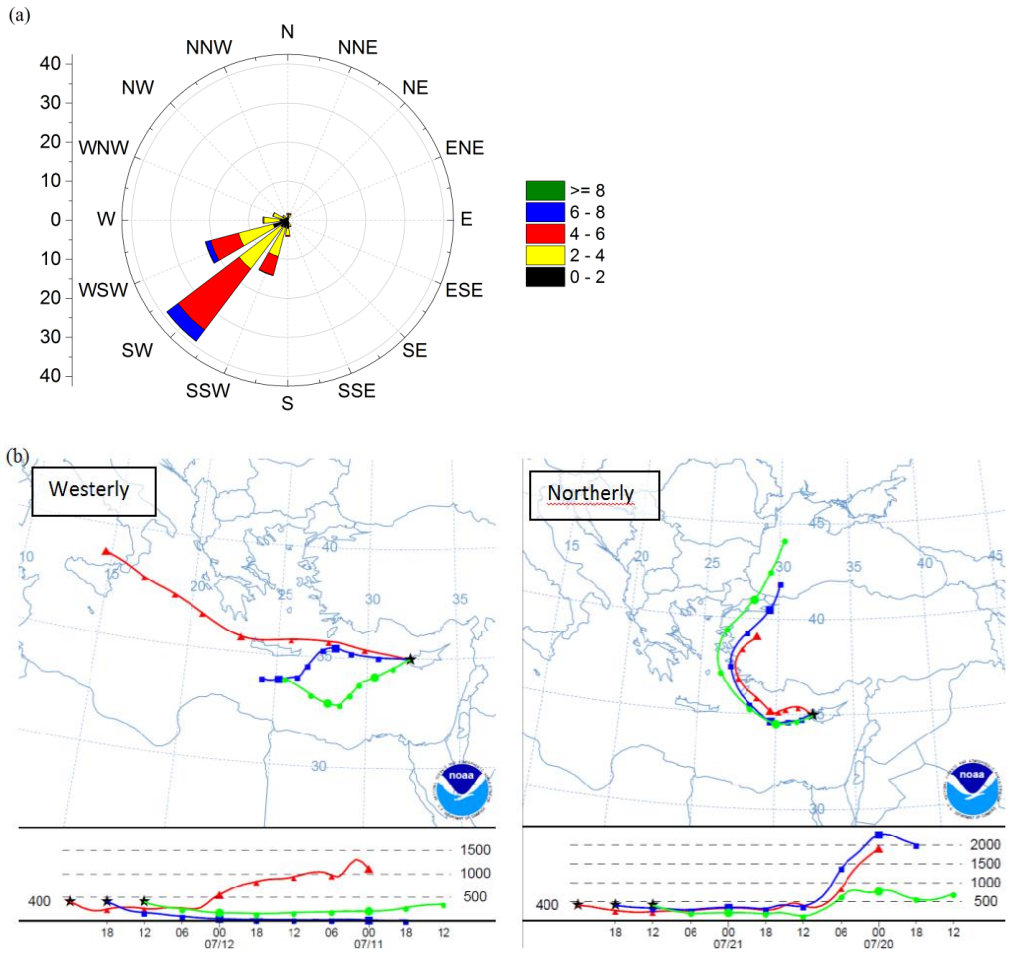


Figure 2: Airflow conditions during the CYPHEX campaign: a) Measured local wind direction, b) back trajectories calculated with NOAA Hysplit model showing examples for the two main air mass origins (48 hours, UTC = LT - 3 h).

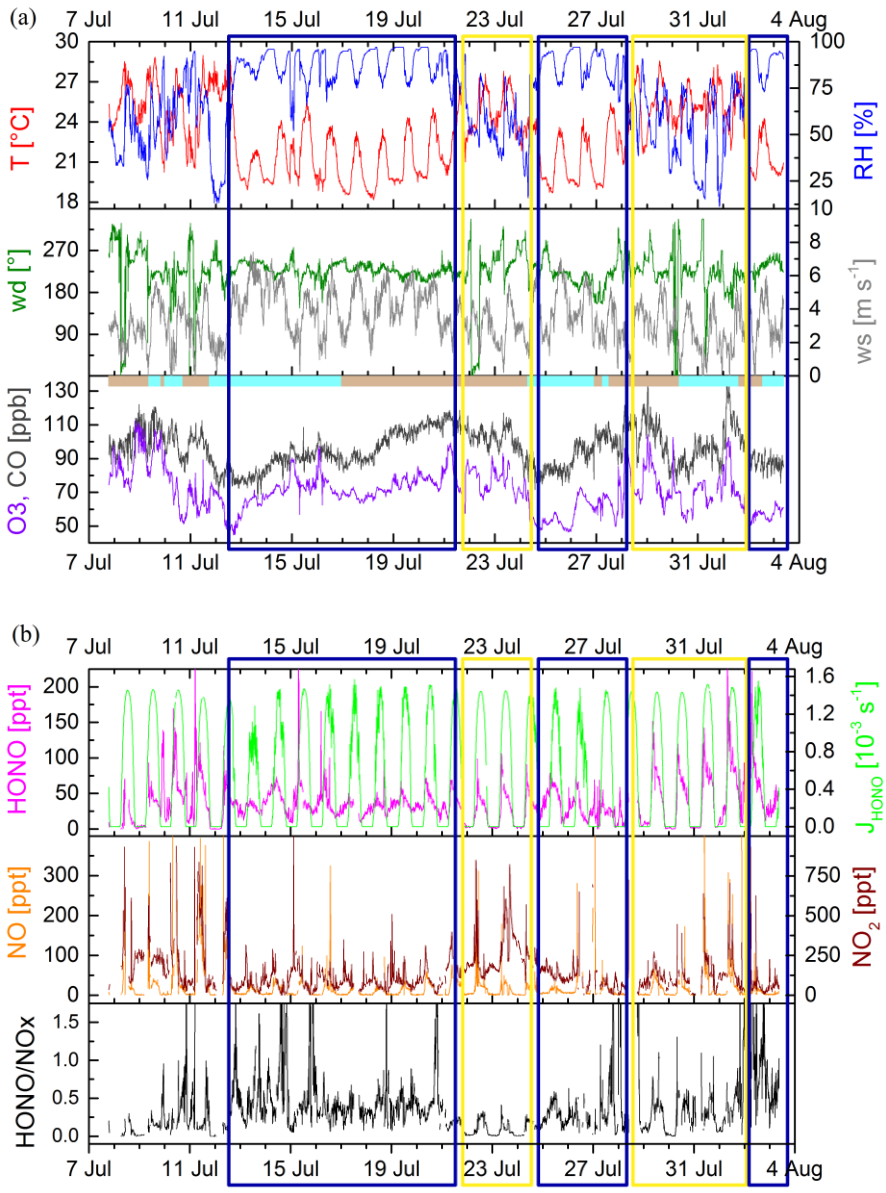
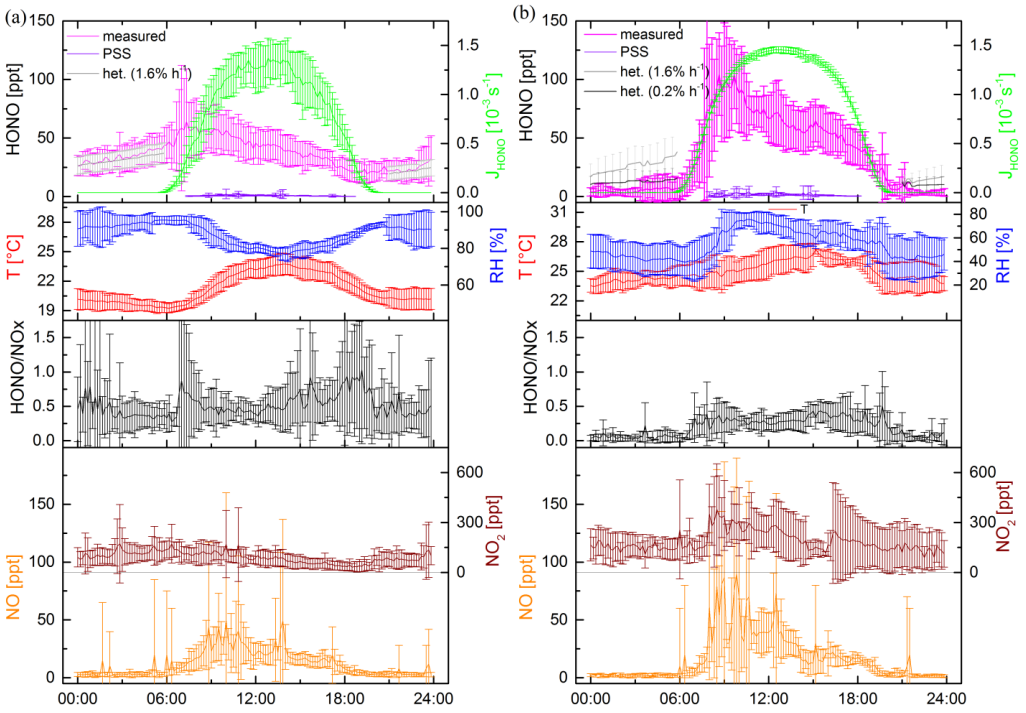


Figure 3: Measured variables during the whole campaign from 7th July to 4th August 2014, a) meteorological data (Temperature T, relative humidity RH, wind direction and speed wd, ws) and O_3 and CO indicating stable conditions, in the lower panel the bar indicates the air mass origin: bright blue = westerly, brownish = northerly, b) observed mixing ratios of HONO, NO_2 and NO, and the photolysis frequency J_{HONO} and the HONO/NOx ratio. The yellow and blue boxes reflect the dry and the humid periods, respectively.


(a)
(b)
measured
PSS
het. (1.6% h-1)
het. (0.2% h-1)
HONO [ppt]
J_HONO [10-3 s-1]
T [°C]
RH [%]
HONO/NOx
NO [ppt]
NO2 [ppt]
00:00
06:00
12:00
18:00
24:00

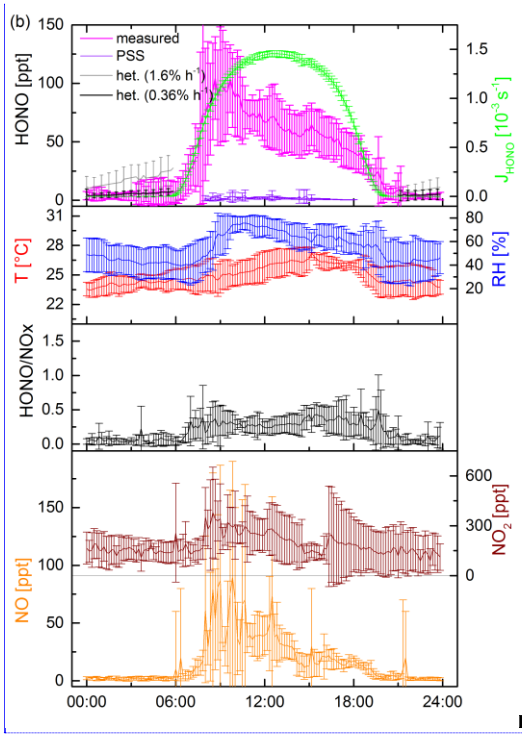


Figure 4: Diel variation of meteorological data (Temperature T, relative humidity RH), NO and NO_2 mixing ratios, the photolysis rate for HONO J_{HONO} and HONO mixing ratios (pink: measured, violet: daytime photostationary state PSS, grey: nighttime heterogeneous NO_2 conversion) and HONO/NOx ratio for a) average for period when RH was above 60% (blue box in Fig. 3) and b) average for dry period when RH was below 60% (yellow box in Fig. 3). Error bars represent standard deviation of diel mean.

Kommentar [HM1]: Corrected according to reviewer 1 (comment 2): changed "starting" concentration for het. Reaction calculation (both rates); (comment 8) error bars of 0.2% rate are black, and now very small-> so not possible to make it more clear

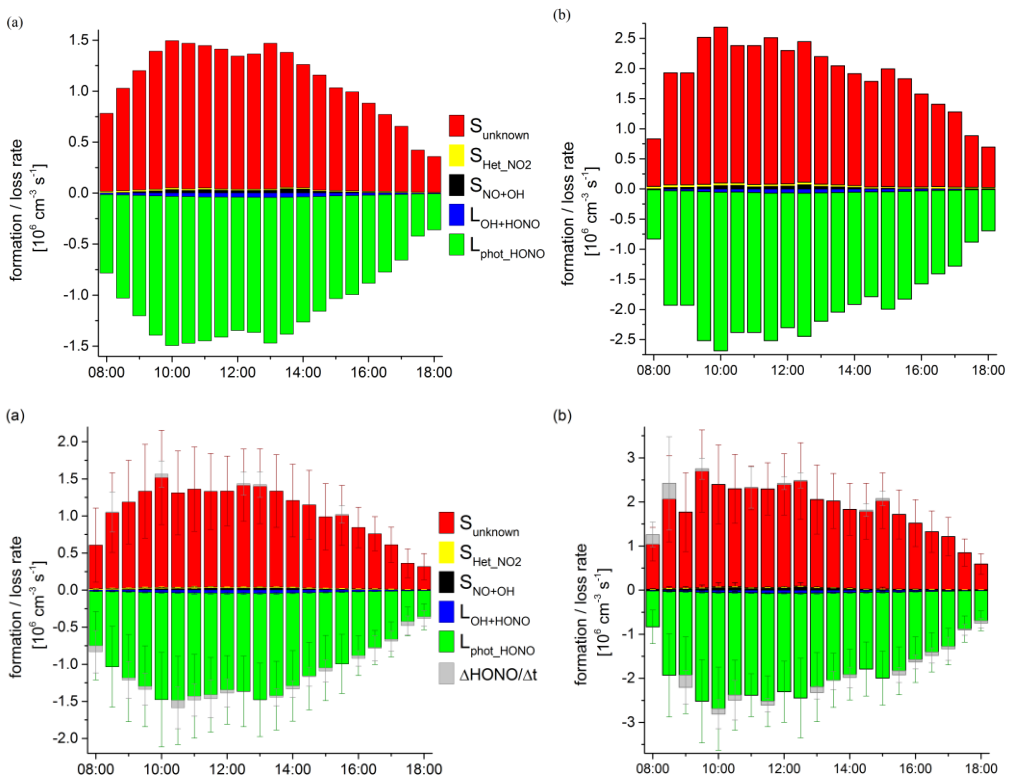


Figure 5: HONO budget analysis for a) the humid and b) the dry period. S_{OH+NO} (black) stands for the formation rate of HONO via the reaction of NO and OH, S_{Het_NO2} (yellow) is the formation rate for the heterogeneous reaction of NO_2 (conversion rate a=1.6% h^{-1}; b=0.36% h^{-1}), L_{phot} (green) and $L_{OH+HONO}$ (blue) are the loss rates via photolysis and the reaction with OH and $S_{unknown}$ is the unknown source. Error bars indicate standard deviation of diel mean.

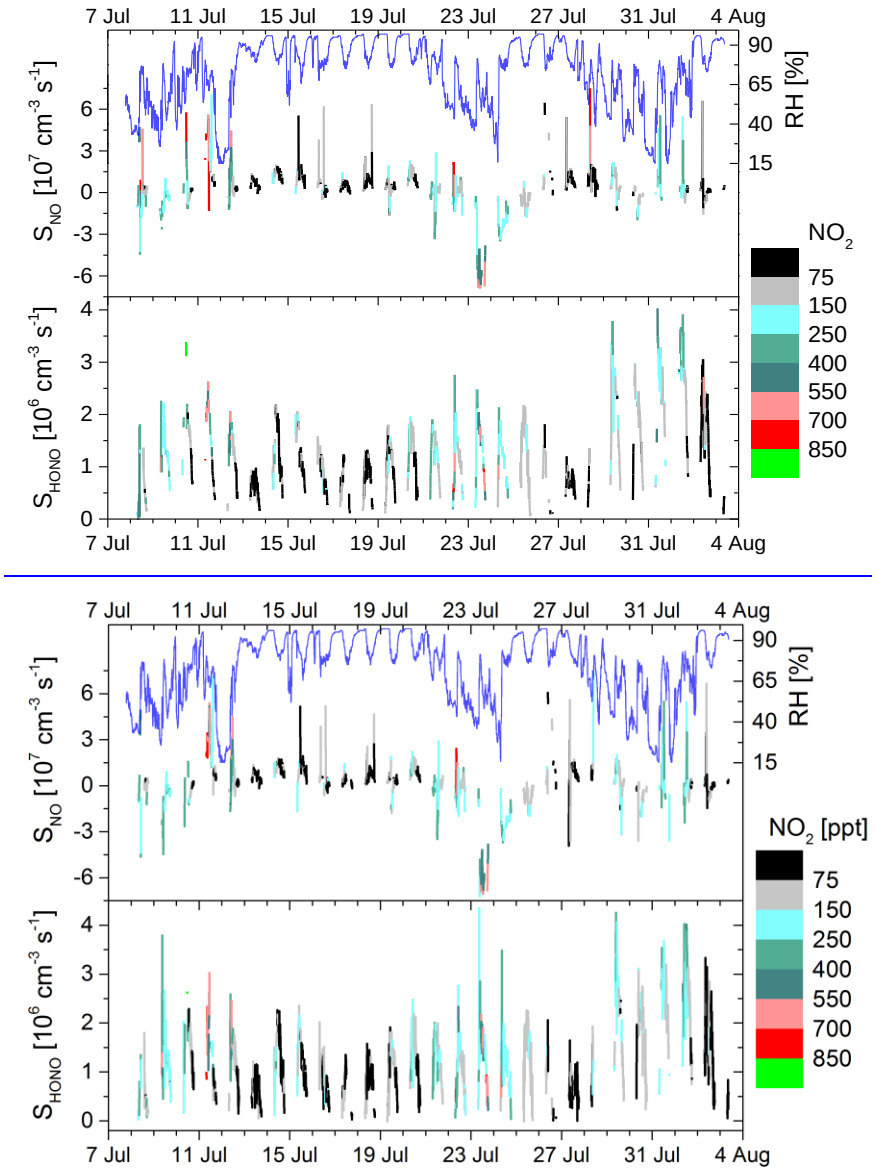


Figure 6: NO_2 (color-coded) and RH dependence of the sources of NO (S_{NO}) and HONO (S_{HONO}).

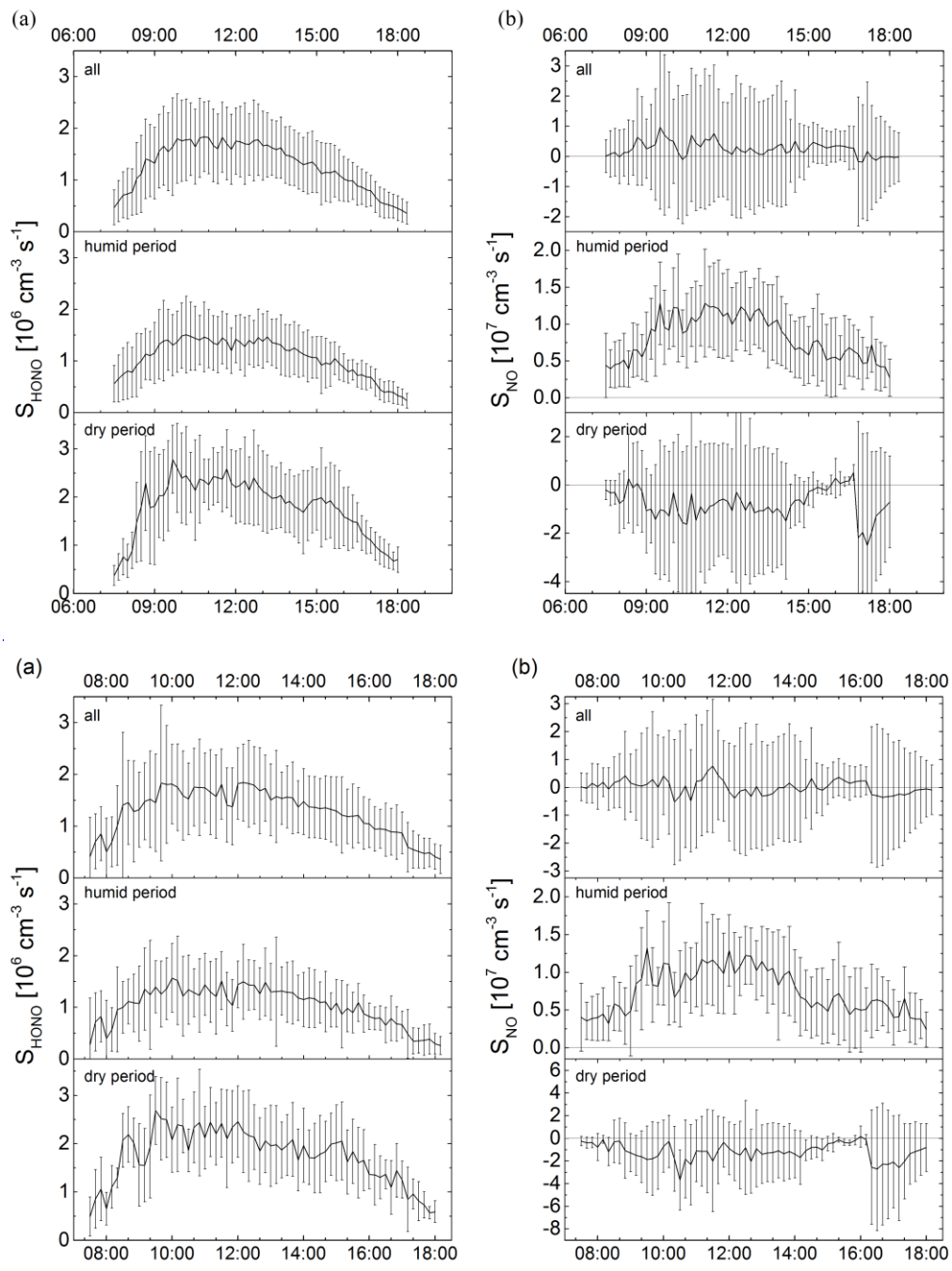
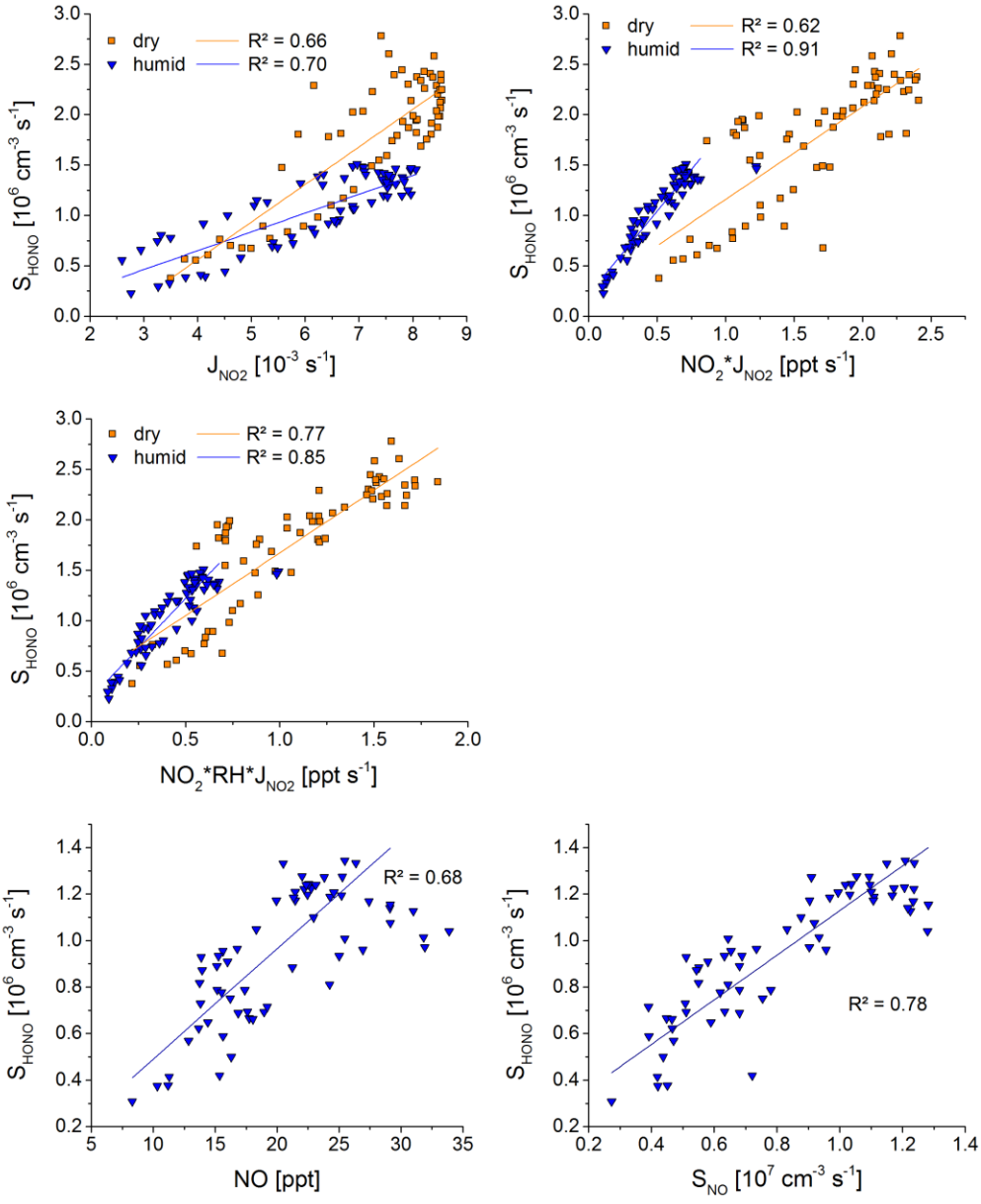


Figure. 7: Diel profile of both unknown sources S_{HONO} (a) and S_{NO} (b) for all data, humid (excluding transition days: 25.7. and 2.8 and 15.7. as RH conditions changed too quickly) and dry periods. Error bars indicate standard deviation of diel average.


dry
humid
R² = 0.66
R² = 0.70
S_HONO [10^6 cm^-3 s^-1]
J_NO2 [10^-3 s^-1]
dry
humid
R² = 0.62
R² = 0.91
S_HONO [10^6 cm^-3 s^-1]
NO2*J_NO2 [ppt s^-1]
dry
humid
R² = 0.77
R² = 0.85
S_HONO [10^6 cm^-3 s^-1]
NO2*RH*J_NO2 [ppt s^-1]
R² = 0.68
S_HONO [10^6 cm^-3 s^-1]
NO [ppt]
R² = 0.78
S_HONO [10^6 cm^-3 s^-1]
S_NO [10^7 cm^-3 s^-1]

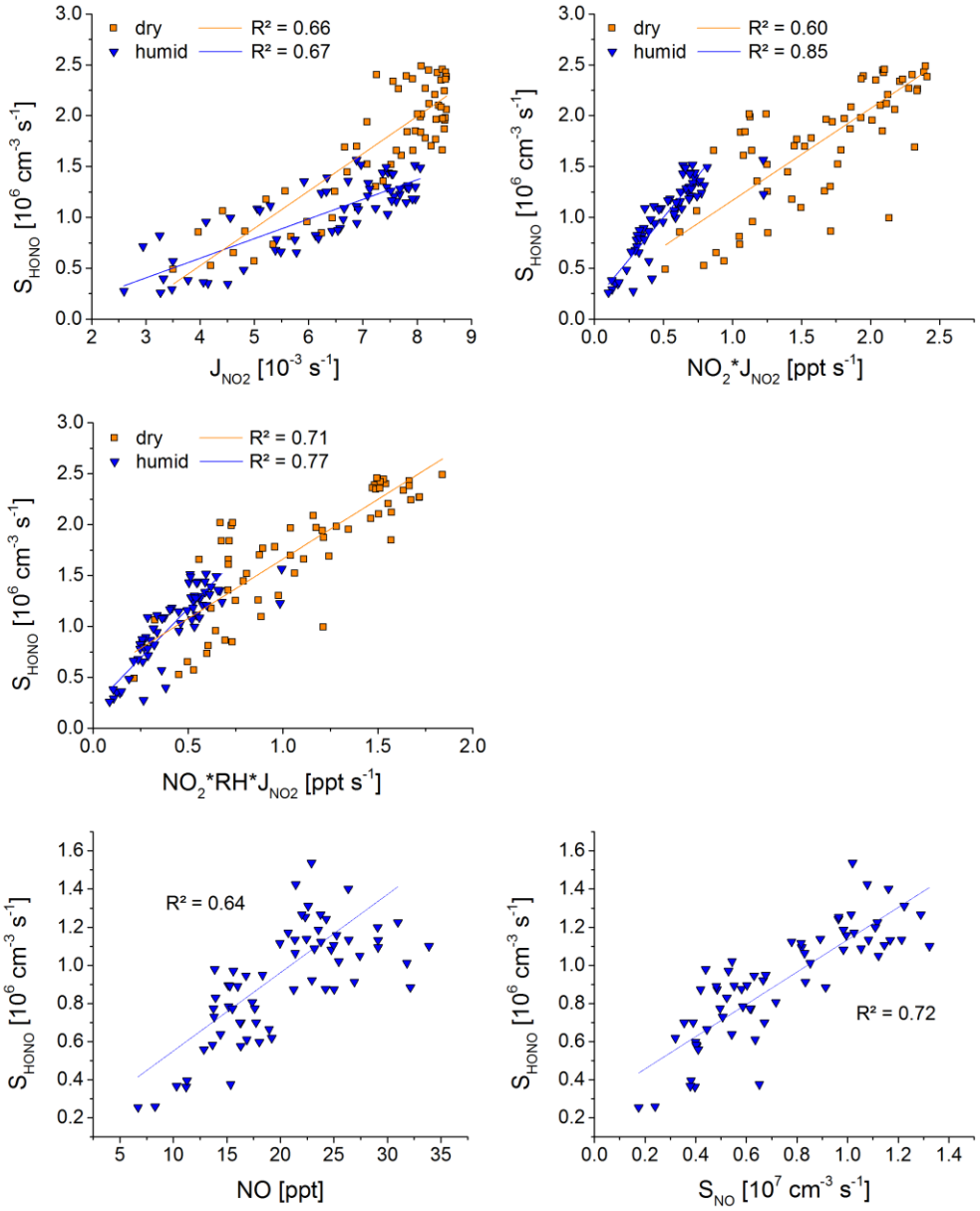


Figure 8: Correlation of S_{HONO} to light induced NO_2 reaction (for both periods, humid = blue triangle, dry = orange square), to NO and S_{NO} (only for humid period, excluding the 3 days mentioned above); time of day average data were used~~d (S_{HONO} and NO; S_{HONO} and S_{NO} excluding the 3 days mentioned before)~~.

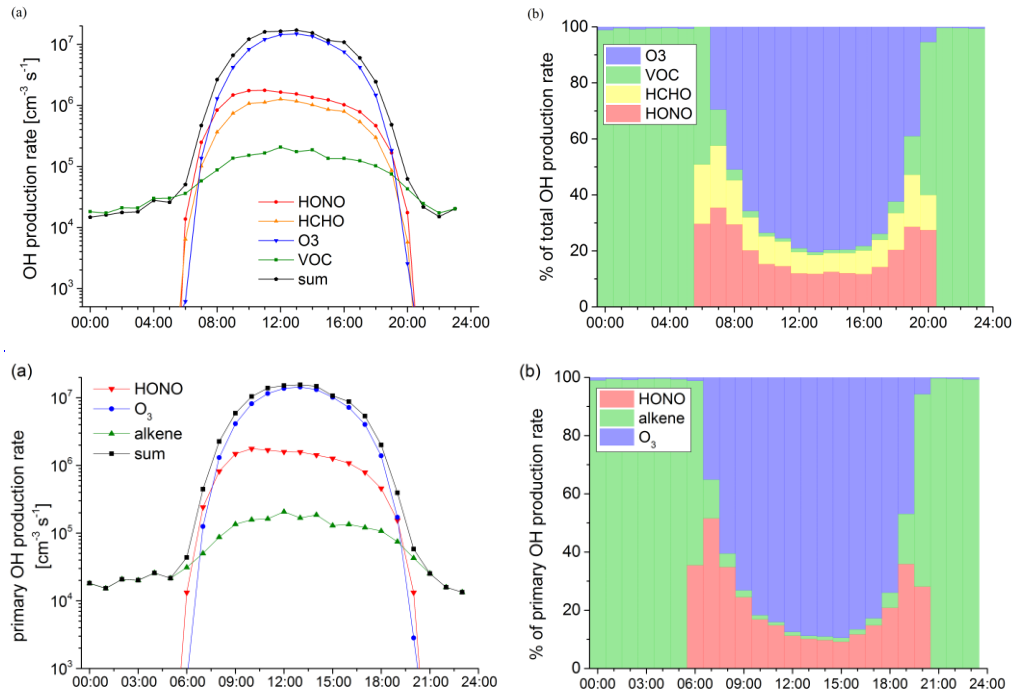


Figure. 9: Average diel pattern of primary OH production from HONO, O_3, ~~HCHO~~ and ~~VOC~~alkenes, ~~a)~~ shown as a) production rate and b) percentage contributions to ~~total~~primary OH production.