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%.

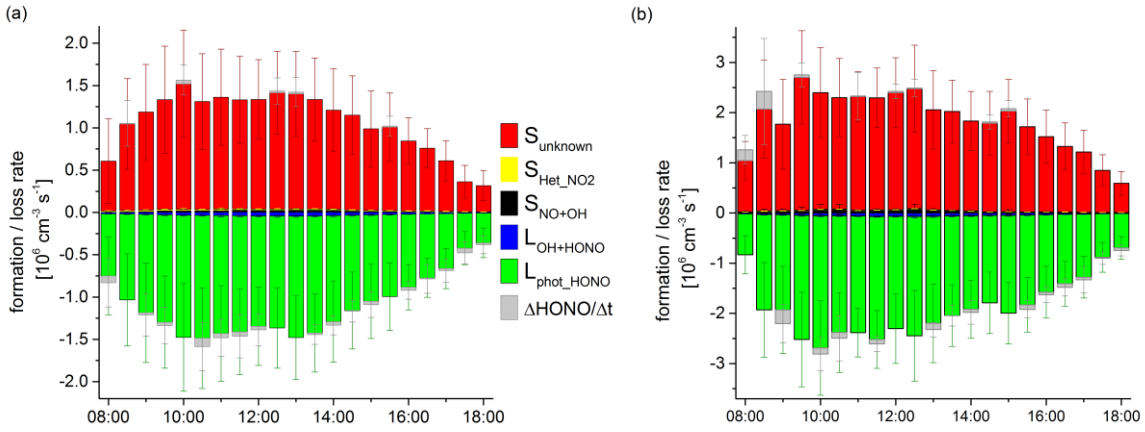
We agree that error bars would help to indicate the uncertainty of the source and sink terms in our calculations. As Fig. 5 a and b show half-hourly mean values of diurnal patterns, we prefer to show the standard deviation of the diurnal mean values as error bars, now included in Fig. 5 a and b, and 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 $4.8x10^5$ 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."

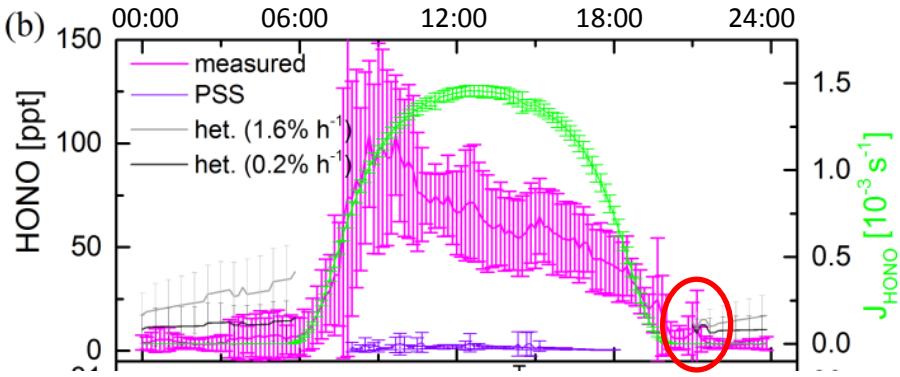
in Fig. 5a/b error bars based on standard deviation of diel mean values are added



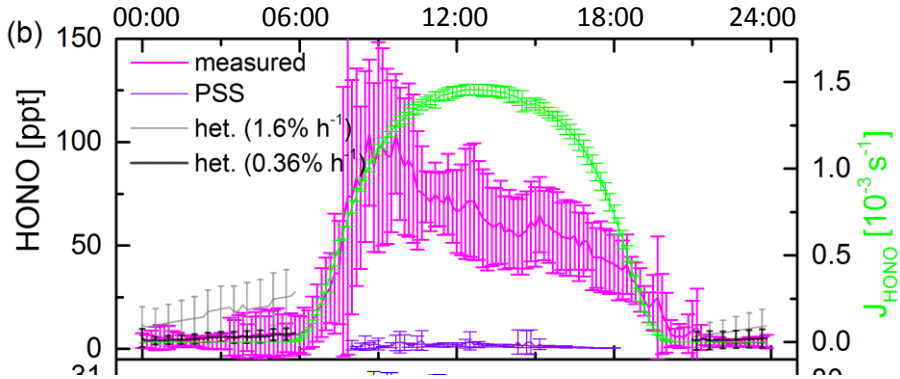
Revised Fig. 5a+b including error bars; as suggested in another comment, the NO_2 conversion rate for the heterogeneous reaction in the dry case (b) is now adopted as suggested by the referee. (ΔHONO/Δt was added as discussed in a comment by reviewer 2)

Specific comment:
In section 5.1, the heterogeneous reaction of NO_2 to form HONO is estimated by applying an NO_2-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 = 1.36x10^{-11} s^{-1}, k_2 = 6.01x10^{-12} s^{-1}, k_3 = 8.96x10^{-12} s^{-1}, k_4 = 1.68x10^{-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)

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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.