Anonymous Referee #3

This paper presented results of flux measurements of HONO over an agriculture field using the gradient method. Based on the averaged diurnal profile, the authors calculated the HONO flux which was then used in correlation studies to explore the contributing mechanism. Photosensitized heterogeneous conversion of NO_2 on soil surfaces were suggested as the major contributor to the HONO flux based on the correlation results and a local parameterization of HONO flux was also proposed. Overall, this is a well-designed study trying to answer the challenging question about atmospheric HONO source. However, there are some important issues that need to be addressed before it is accepted for publication in ACP.
We would like to thank Referee #3 for his/her interest and comments to the manuscript, which are addressed below:

Referee #3:
Major issues:
(1) HONO flux calculation
According to Eq (2), the calculated flux depends on the gradient of HONO at two heights. If the difference between such values is too small, e.g. comparable to the systematic difference of instruments ~2-13% as shown in Fig. 2, it may invalidate most discussions. I would like to see the difference in both absolute and relative term (ΔHONO and ΔHONO/HONO).
Answer:
First, the relative errors of the Δ[HONO] data induced by the agreement between both instruments will be lower than e.g. the 13 % shown for the intercalibration during PHOTONA 3 (see Figure 2), since the results from the intercalibrations were used to harmonize the LOPAP instruments (see lines 196-198). Thus, although both instruments may have a higher absolute uncertainty, after this harmonization the sign of the fluxes will be only affected by the lower precision errors of the two instruments. In addition, in the revised manuscript, we will add all Δ[HONO] data including their precision errors in a modified Figure 3 (whole campaign data). In contrast in Figure 4 (average days, from which all correlations are derived), presentation of campaign averaged Δ[HONO] data (and their errors) would not be directly comparable to the shown standard errors ($\sigma/\sqrt{n}$) of the campaign averaged HONO fluxes, since the average fluxes were not calculated from the campaign averaged Δ[HONO] data, but present the averages of the individual fluxes over the whole campaign (see also next point). The flux standard errors were typically much lower than the fluxes and thus, the observed trends are statistically significant (see flux error bars in the figures).

Referee #3:
The authors used averaged values to interpret the flux data: "*To interpret the flux data for each measurement campaign, a diurnal average was calculated by the formation of one-hour means from the whole measurement period.*" My question is how did you average and, etc, since their expression is different between stable and unstable conditions. In principle, it is a question whether we should first calculate the flux at each time and then do the averaging, or first do the averaging of individual parameters and then calculate the flux. Can the authors address this issue and try to make calculation for both cases?
Answer:
Unfortunately, this point was not described clearly enough in our manuscript (see also same question by referee #1). Here first, 30 min (PHOTONA 1 and 2) or 5 min (PHOTONA 3) averaged campaign flux data were calculated using different stability integrated functions Ψ for stable and unstable conditions (see supplement). Secondly, single 24 h average campaign days (hourly data) were derived for each campaign after filtering the campaign data for untypical events (rain, high pollution plumes, see section 2.4).
To clarify the averaging procedure, we modified in section 2.4 (Data treatment):
"To interpret the flux data for each measurement campaign, first 30 min (PHOTONA 1 and 2) or 5 min (PHOTONA 3) averages were formed from the measurement data including the HONO fluxes. Secondly, for each campaign a diurnal average day using all this averaged data was calculated by the formation of one-hour means from the whole measurement period."

Referee #3:
My last question is if the effect of chemistry can be neglected in the calculation of HONO fluxes. We can make a simple HONO budget expression around noon time as follows,
$\partial HONO/\partial t = \partial F/\partial z + S$
in which the change of HONO concentration ($\partial HONO/\partial t$) is subject to the gradient of flux ($\partial F/\partial z$) and the photolytic loss term (S). If $\partial HONO/\partial t \ll S$, then the contribution of S should be comparable to flux ($\partial F/\partial z$) and cannot be neglected.

Answer:

This point is already considered in section 2.5.3 in which we exactly investigated the proposed concern. By comparing the photolytic lifetime of HONO as the fastest HONO chemical term with the transport time (see equations 4 and 5) the influence of the chemistry on the HONO fluxes were found to be less than 10 % and thus any correction for chemistry was ignored (see lines 239-243).

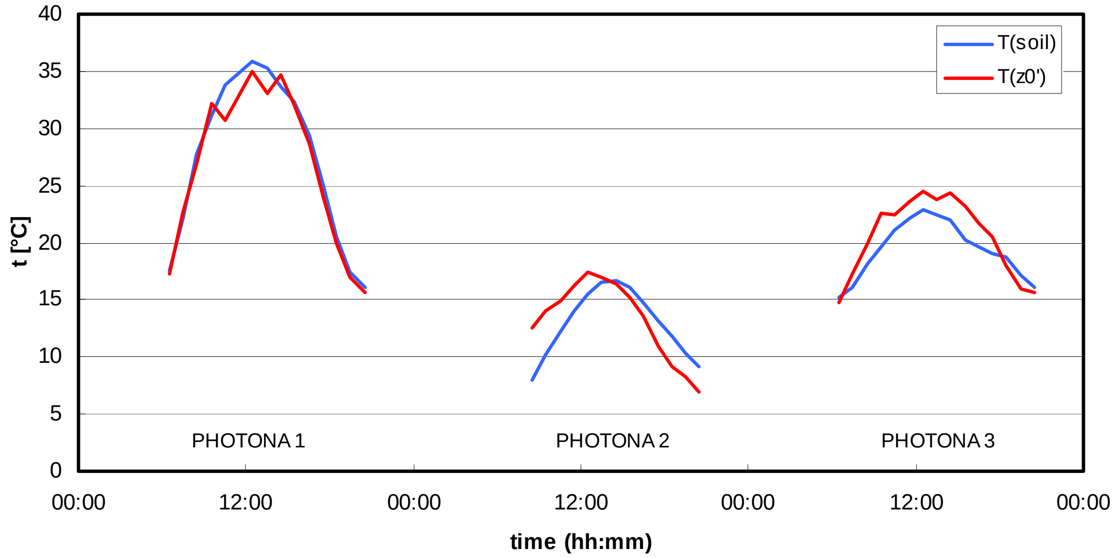
Referee #3:

(2) Soil surface emission

The diurnal course of soil temperature strongly depends on the depth. Here the authors used soil temperature at 5 cm in their calculations. I would suggest using soil surface temperature as in Su et al. (2011) which is more relevant for soil-atmosphere exchange. Figure 1 of Su et al. also suggests that HONO produced by photo-sensitize reaction (on the surface) is subject to the temperature dependent equilibrium. Since the peak of soil surface temperature appears earlier than that of deeper soil (see the following figure, Jury and Horton 2004), the correlation with HONO fluxes might be improved.

Answer:

We generally agree to that issue and especially temperatures at deeper soil layers show significant different diurnal profiles compared to the surface temperature. However, in our case the measured soil temperature a 5 cm depth was not too different compared to the theoretical surface temperature $T(z_{0'})$, see Figure below.



Especially for PHOTANA 1, the daytime profiles were almost the same and for PHOTONA 3 at least the shape and the timing of the maximum temperatures were also quite similar. Only for PHOTONA 2 the diurnal profile of $T(z_{0'})$ was shifted slightly to earlier daytime as shown by the referee by the data from the study of Jury and Horton (2004). Despite the similar shapes of the diurnal temperature profiles, especially for the two summer campaigns, we have repeated the correlation analysis using also the proposed surface temperature. As expected, the use of $T(z_{0'})$ did not improve the quality of the correlations compared to the use of the directly measured soil temperature, see blue numbers in the following table.

Table 1: Goodness of the weighted orthogonal regressions of hourly average daytime data (6:00 to 20:00 UTC) of *F(HONO)* against different variables for the three PHOTONA campaigns. The numbers represent χ^2/Q (R^2) values for which lower χ^2 and higher Q and R^2 values indicate better correlations (for definition see Brauers and Finlayson-Pitts, 1997). Bold numbers represent the strongest correlations observed for each campaign. Data for the correlation using the theoretical surface temperature $T(z_{0'})$ is added in blue.

	$J(NO_2)$	$J(O^1D)$	T_{soil}, $T(z_{0'})$	u_*	$J(NO_2)\cdot c(NO_2)$
PHOTONA 1	27.5/0.004 (0.47)	not measured	$50.2/6\cdot10^{-7}$ (0.22) $46.4/3\cdot10^{-6}$ (0.21)	23.4/0.016 (0.41)	**7.27/0.78 (0.79)**
PHOTONA 2	12.1/0.28 (0.27)	not measured	9.33/0.50 (0.019) 8.5/0.58 (0.29)	**5.66/0.84 (0.37)**	12.4/0.26 **(0.37)**
PHOTONA 3	$53.7/3\cdot10^{-7}$ (0.38)	$79.8/5\cdot10^{-12}$ (0.17)	$121/5\cdot10^{-20}$ (0.03) $91.9/2\cdot10^{-14}$ ($4\cdot10^{-7}$)	$62.7/7\cdot10^{-9}$ (0.20)	**3.26/0.994 (0.85)**

Since the correlations of the HONO flux with $J(NO_2)\cdot c(NO_2)$ were still much better compared to those when using $T(z_{0'})$, see bold data, our conclusion is not affected by the use of the different temperatures. Since in addition $T(z_{0'})$ is a theoretical temperature showing some degree of uncertainty, we prefer using the directly measured soil temperature at the lowest depth of 5 cm.

Referee #3:
Minor comments:
Ln 22: "unusually high" suggests that the measured values is higher than the expected values. Many of the references, however, don't really have an expected value from modeling or budget analysis. Thus I suggest modifying the text or limiting the references to those with budget analysis. The following references should be included into the reference list (Su et al 2008, Li et al. 2012, Yang et al. 2014).
Answer:
We will add two of the suggested references to the revised manuscript (there are too many on this topic…), while the one by Yang et al. (2014) was already used. However, we also would like to show the long history of the proposed missing daytime HONO source starting with the first study by Neftel et al. (1996). Already in this study a clear missing daytime HONO source was identified, although the authors could not make a complete budget analysis, caused mainly by the missing measured OH (which is by the way also not available in the proposed study by Su et al.). However, whatever reasonable OH data is used in most former calculations, the measured daytime HONO would be not in balance with its known sources and sinks. E.g. in the first study in which all necessary parameters were measured to answer this issue (Kleffmann et al., 2005), a completely unreasonable, more than an order of magnitude higher OH concentration would have been necessary to get the PSS similar to the measured HONO (=> "unreasonably high"). Thus, also former studies already proved the existence of a daytime source of HONO, although with higher uncertainty in the absolute magnitude.

Referee #3:
Ln 30: "bacterial production of nitrite in soil", it is better to say "biogenic production of nitrite in soil"
Answer:
Will be changed in the revised manuscript.

Referee #3:

Ln 42: "calculated daytime HONO sources, determined from HONO levels exceeding theoretical photostationary state (PSS) values, showed high correlations with the photolysis rate coefficient *J*(NO_2) or the irradiance and NO_2 concentration (Elshorbany et al., 2009; Sörgel et al. 2011b; Villena et al., 2011; Wong et al., 2012; Lee et al., 2016)." So far as I know, Su et al. (2008) is the first study performing such correlation analysis and is unfortunately missing from the reference list.

Answer:

We will add the suggested reference, which we originally not used, since J(NO_2) was not measured in that study and was calculated by the TUV model, which might be uncertain under the high aerosol load and the corresponding influence of light scattering on the UVA levels under these highly hazy Chinese (Beijing) conditions. In addition, a J(NO_2) dependent daytime source was already used in a former study (Vogel et al., 2003), which we now also added to the references besides the most recent one by Crilley et al. (2016).