Anonymous Referee #1

This is an interesting manuscript; it presents some valuable information and discussion on HONO sources over an agricultural field site. It is suitable for publication in ACP. Here are my general comments and questions:

We would like to thank Referee #1 for his/her interest and comments to the manuscript which are addressed below:

Referee #1:
It is surprising that microbial nitrite formation in the soil is only a minor contribution to the overall HONO emission from the ground; it is expected to be a major one over actively farmed and heavily fertilized areas such as the study site. Were soil acidity/alkalinity and nitrite content measured during the campaign? Soil (and the ground surface) acidity/alkalinity is one of the most important factors controlling the direction and the rate of HONO exchange between the air and the soil (and the surface).
Answer:
During the individual campaigns soil nitrite and pH were unfortunately not measured, since the microbial soil source was still not discussed at the time of the PHOTONA campaigns. However, later for the study of Oswald et al. (2013) soil samples from the PHOTONA field site were collected and analyzed for nitrite, pH and optimum HONO fluxes in the lab. This lab data, parameterized for humidity and temperature by Oswald et al. (2013), was used here to calculate potential HONO fluxes for the individual PHOTONA conditions, which were of the same order of magnitude of measured HONO fluxes only during PHOTONA 1, but were completely negligible for the other two campaigns (see section 3.2). Reasons for the variable theoretical HONO emissions by the soil source are the extremely dry conditions required for the optimum HONO fluxes based on the lab experiments of Oswald et al.. Low soil water content (SWC) was partially present only during PHOTONA 1 (and even here the SWC was still a factor of two higher compared to the optimum humidity in Oswald et al.). In contrast during PHOTONA 2 and 3 the soil was too humid to allow any significant HONO emissions from bulk soil processes. In contrast to these theoretical estimations, experimental HONO fluxes were quite comparable, especially during the two summer campaigns PHOTONA 1 and 3. Since it is unreasonable that only the soil source was the main reason for the observed HONO fluxes in PHOTONA 1, while only other sources were active during the other two campaigns, and since the correlation results are in contradiction to this source, also for the dry PHOTONA 1 campaign, we do not think that microbial nitrite production was the major origin for the observed HONO fluxes (see also the detailed discussion in section 3.4).
It should by highlighted that in the lab experiments of Oswald et al. soil samples are flushed by completely dry air which is a quite different situation compared to a typical humid atmosphere (30-100 % r.h.). Thus real HONO fluxes by the microbial soil source in a humid atmosphere might be much lower compared to these lab derived optimum HONO fluxes. Here more realistic lab experiments under atmospheric conditions are required for the future. In conclusion, the experimental field results from the present study do not confirm the proposed microbial HONO source, similar to other field studies, see e.g. Oswald et al. (2015).

Referee #1:
The authors should assess and discuss the contribution from ground emission to the overall HONO budget in the atmospheric surface boundary layer. Based on my very rough calculation, this contribution is ~30% at the noontime, assuming [HONO] ~200 pptV, J(HONO) ~1.1×10^{-3} s^{-1} (~15 min photolysis lifetime), F(HONO) ~5×10^{13} molec m^{-2} s^{-1}, and a surface mixed layer height of ~30 m. The vertical mixing is enhanced by surface heating during the day in summer, and HONO emitted from the ground surface may be transported up to several hundreds of meters above the ground level within its photolysis lifetime.
Answer:
The suggested calculation would be only possible using a 1-D vertical chemical transport model including meteorological information (e.g. height-dependent vertical mixing in the boundary layer, BLH, etc.) and additional chemical data (e.g. OH radical vertical profiles to calculate NO+OH contribution to the HONO levels (PSS) and vertical HONO profiles in the BL), which we do not have. Without such information calculations on the contribution of the ground source to HONO levels in the BL would be highly speculative (and height-dependent, contribution will gradually decrease to zero with increasing height…) and are in addition also out of the scope of this experimental field study.

Referee #1:
The measurement data of each campaign were lumped into 24 1-hr diurnal averages and then the fluxes were calculated.
Answer:
Our average campaign flux data used for the correlation analysis was determined differently than the referee concerned. First, 30 min (PHOTONA 1 and 2) or 5 min (PHOTONA 3) averaged campaign flux data was calculated and evaluated for potential correlations. Since this was not very successful (see below), secondly, single 24 h average campaign days 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 #1:
The authors argue that this averaging process reduced the errors of measurements for each parameter. However, a lot of detailed and valuable information was lost. If the data were averaged for each 1-hr interval, not lumped over the whole campaign, the authors may not need to filter out those "highnoise" data points and may be able to see real changes in HONO exchange direction and magnitude with many environmental factors during different events (e.g., rainy vs sunny, clean periods vs pollution episodes,…).
Answer:
Here the referee is generally right that the analysis of individual variable diurnal data could have gained deeper information on the HONO sources. However, we decided not to use the individual data caused by several reasons:
a) There were many gaps in the individual data for which all instruments were simultaneous in operation (different zeroing, calibrations, malfunctions, etc.). Thus, in potential diurnal correlations the data coverage would have been different from day to day (e.g. start and end time of the available data, no complete rainy/sunny days, etc.) which would lead to a comparison of apples and oranges. In contrast, for the used average diurnal day (using all simultaneous campaign data) full 24 h data is available for each campaign.
b) The collected vertical gradient data showed low stationarity, which is an important criterion to analyze individual gradient data. A test for stationarity as described by Foken and Wichura (Agricultural and Forest Meteorology, 78, 83–105, 1996) showed that up to 80 % of the flux data were collected under non-stationary conditions. Here the precision of individual flux data for short specific periods (rainy/sunny/polluted) would be not very high and would not allow the interpretation of these specific short events, even if complete diurnal data were available (see a). In contrast, the use of the campaign averaged diurnal day significantly reduced the scatter of the data and showed more precise trends of the diurnal HONO flux and its correlations with $J(NO_2)$ and NO_2.
c) Although for short periods different processes may have been active, the aim of this study was to identify major processes describing our average daytime flux data, for which a photosensitized conversion of NO_2 is a more reasonable candidate than e.g. the microbial soil source, although the latter may still have been active with a much smaller average contribution or for short individual periods (see discussion in section 3.4).

Specific comments:
Referee #1:
P13, L475: "nigh-time" should be "nighttime".
Answer:
Changed, but we used the form with the hyphen, similar to the rest of the text. In addition, we changed night time to night-time in line 260.

Referee #1:
Figs. 3 and 4, HONO gradient: HONO concentrations were measured at two heights; which one is shown in the figures? One important parameter in HONO flux calculation is the difference in HONO concentrations at the two heights (Δ[HONO]). Please plot the concentrations at both heights or the Δ[HONO]. The precision of F(HONO) is directly dependent on how significant the difference between the two concentrations; the difference between two similar numbers would result in a small number with a large relative uncertainty (i.e., Δ(gradient) » Δ[HONO]). Readers need the information to assess the accuracy of the calculated F(HONO).

Answer:
In Figure 3, where the complete campaign data are shown, the upper level data is presented. Here mainly the range of situations should be presented in a similar way like in other typical HONO field campaigns, where HONO and potential precursors are collected typically in a few meters altitude above the ground. In contrast, for the correlation analysis for which the campaign average days are used (see Figures 4-7) the lower level data is presented. Using this data, source processes which are proposed to take place on the ground surfaces are better described. The exception is PHOTONA 3, where NO_x was measured only in one altitude (see experimental section). We will specify the measurement levels in the revised manuscript.
In addition, 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), presentation of campaign averaged Δ[HONO] data (and their errors) would not be directly comparable to the shown precision errors of the campaign averaged HONO fluxes, since those fluxes were not calculated from the campaign averaged Δ[HONO] data, but present the averages of the individual fluxes over the whole campaign (see explanation to the concern above). The size of the flux errors were typically much lower than the fluxes and thus, the observed trends are statistically significant (see flux error bars in the figures).

Referee #1:
Fig. 6: Several high F(HONO) data points for the morning hours should probably removed, since they may be caused by the release of trapped nitrite in dew (p 14, L 500-503). The removal of these odd data points seems to significantly improve the correlation between F(HONO) and T(soil). Would the improved F(HONO) - T(soil) correlation suggest that soil emission (from microbial nitrite formation) may be more important after all?
Answer:
Since the controlling influence of F(HONO) by $J(NO_2)$ and NO_2 (see Fig. 5 and Tab. 1) is not considered in Fig. 6, the scatter of a simple plot of F(HONO) against only the temperature is obviously high. Thus, the high F(HONO) data in Fig. 6, e.g. for PHOTONA 3, are no "outliers" (by any dew evaporation) but simply reflect the different NO_2 and radiation levels for the same temperature (compare Figure 7, where these controlling factors are included). In contrast, the correlation with $J(NO_2)\times NO_2$ was excellent for PHOTONA 3 (see Tab. 1). In addition, only the one high F(HONO) point for PHOTONA 2 (ca. 8×10^{13} molecules m^{-2} s^{-1}, see Fig. 6 and Fig. 4) was explained here by dew evaporation at the very low morning temperatures of this spring campaign (see cited discussion). However, the removal of only this single point will not change too much the regression results using all data. Furthermore, since dew formation was not quantitatively studied (so the explanation of the morning peak during PHOTONA 2 is speculative and only based on results from other field studies) it would be completely unclear which data points have to be removed (by different filtering we could get almost any slope in Figure 6…). Finally, since we later described all flux data (including the night) by the equation (8) – using also a temperature dependent term – we decided to use all data in Figure 6.
In contrast, for the correlation results of the individual campaign data (see Fig. 5 and Tab. 1) the morning peak during PHOTONA 2 was already removed from the daytime data as suggested by the referee (here only the data 8:00-20:00 was used while it was 6:00-20:00 in PHOTONA 1 and 3, see text). Thus, the correlation results were already filtered for this unusual high morning peak during PHOTONA 2 and still the results point to a radiation and NO_2 dependent source.

Referee #1:
Fig. 6 caption: check the equation; a left bracket is missing.
Answer:
Thanks for pointing to this typo. But one bracket was deleted and not added; compare the equation in the figure.

Referee #1:
Supplemental, L7-10: Why both equations (S1) and (S2) are under "unstable conditions"? One should be for stable and the other for unstable conditions. Please cite the reference for each condition.
Answer:
The typo was corrected and the two references are valid for both cases which will be clarified in the revised manuscript. In addition, we corrected equation (S2) for another typo:

$$\Psi_{(z-d)/L} = 2\cdot ln\left[\frac{1+\sqrt{1-16\cdot\frac{(z-d)}{L}}}{2}\right] \qquad \text{(S2)}.$$