Anonymous Referee #2

This paper describes three field investigations into the surface emission fluxes of nitrous acid (HONO) above soil / low crops in France. This topic relates to a series of recent studies which have demonstrated that additional fluxes of HONO to the boundary layer (beyond gas phase / heterogeneous reactions and dark NO_2/H_2O interactions) are required to explain observed daytime steady-state HONO levels. This is of importance as HONO is an important precursor to OH in many continental boundary layer settings, and the paper addresses a current high profile topic in atmospheric chemistry using state-of-the-science approaches.

HONO fluxes were measured using the gradient method, employing a pair of LOPAP monitors sampling at different heights above the soil / crops. The resulting fluxes are found to be comparable in magnitude to those inferred previously (although HONO flux observations are few and far between), and significantly larger than those which would be inferred by the temperature and soil moisture dependence of biotic emissions from previous laboratory studies (but see my comments below).

The correlation between the observed flux and some potential controlling factors are observed, and the best correlation obtained for NO_2, photolysis (jNO_2), and temperature, adjusted for RH. This result is qualitatively attributed to photoenhanced NO_2 conversion to HONO upon humic-acid type surfaces.

The paper is well written (a few minor language suggestions are given below) and clearly phrased / easy to follow. The experiments are clearly described and analysed (NB suggestions for a couple of expanded explanations below) and the conclusions, although correlation rather than definitive causation, are reasonable and advance our understanding. Subject to the points below being satisfactorily addressed, I recommend publication in ACP.

We would like to thank Referee #2 for his/her interest and comments to the manuscript, which are addressed below:

Referee #2

Minor points

L48 PSS also fails where there are significant heterogeneity in the co-reactants of the species in the PSS – notable OH – i.e. significant heterogeneity in VOC loading causes problems for HONO PSS analyses, even if the NO and HONO components are in a homogeneous environment.

Answer:

Typically, when calculating a missing HONO source by the PSS approach, only the photolysis of HONO, its reaction with OH and the back reaction NO+OH are considered (some studies in addition also consider the dark conversion of NO_2 on surfaces). To calculate the theoretical HONO steady state concentration only J(HONO), k(NO+OH), NO and OH (and NO_2) are necessary. From the difference of the measured HONO to this PSS concentration a missing HONO source is calculated. Since the lifetime of the OH radical is less than a second, heterogeneity in the OH is not an issue (for OH the PSS approach is perfect…) and only heterogeneity of HONO and NO (and NO_2) add a significant uncertainty. Thus, any heterogeneity in the VOC loading is not an issue. The VOC loading certainly affects OH, but this is perfectly accounted for when using measured OH. In conclusion, we feel that the uncertainties of the PSS approach are well summarized by the cited study of Lee et al. (2013). For completeness we have added the very recent paper by Crilley et al. (Faraday Discussion 189, 191, 2016) as another reference to this topic.

Referee #2

L103 the key for PNA (HNO_4) interference in the flux measurements is not the absolute amount but the different in PNA across the flux measurement heights. Can the authors comment on this.

Answer:

We totally agree. Since the HONO flux is calculated from the difference of the HONO signals of both LOPAP instruments only the difference in a potential HNO_4 interference between both instruments will be important. Thus, the stated 15% interference of the upper limit HNO_4 level of <50 ppt (<7.5 ppt interference) is an upper limit, since it is not expected that the HNO_4 level at the lower LOPAP will decrease by dry deposition to 0 % of the upper instrument. For further clarification we will add: “In addition, since HONO fluxes are calculated only from the difference of both instruments, potential HNO_4 interferences are not considered important in the present study.”

Referee #2

L111 It is not appropriate to “ignore” the potential interference – please calculate (estimate) the anticipated PAN levels making reasonable assumptions and hence quantify the potential interference in the NO_2.

Answer:

Unfortunately, we (a) do not know the magnitude of the PAN interference of our Luminol NO_2 instrument (we do not have access to a PAN-GC…) and (b) we have not measured the VOC loading during the PHOTONA field campaigns. Thus, we are not able to calculate/model potential PAN concentrations/interferences during our field campaigns. By the way, also the Ecophysics NO_x instrument (used here for NO, but is typically also used for NO_2) has a significant PAN interference caused by the warm photolytic converter and its long residence time of ca. 10 s, see the recent ACP paper by Reed et al. (Atmos. Chem. Phys., 16, 4707–4724, 2016). Caused by the proximity to the Paris urban region and the expected average transport time of NO_x, we do not expect high overestimation of NO_2 by PAN interferences. And even if we had significant PAN interferences in the present study, the higher expected PAN levels in the early afternoon (photochemically formed) could not explain our maximum HONO fluxes in the morning. Thus, the qualitative result (correlation of the HONO flux with $NO_2 \times J(NO_2)$ would not have negated by such an interference. It is even the opposite, if potential PAN interferences were corrected (=> the daytime NO_2 profile would get than even more asymmetric, see Fig. 4) the correlation of the HONO flux with $NO_2 \times J(NO_2)$ would have increased compared to the other proposed HONO sources, which are expected to maximize in the early afternoon (see discussion in section 3.4).

Referee #2
Section 2.3 – how well was the stability criterion satisfied – what fraction of the data had to be discarded?
Answer:
The fraction of time with Obukhov length lower than 5 in absolute value was 24 %, 21 % and 16 % in 2009, 2010 and 2011, respectively, while very unstable conditions ($L < 0$) occurred 13 %, 12 % and 7 % of the time, respectively. We however did not filter the data for stability, as stable conditions also generally corresponded to small fluxes, and we rather wanted to consider as much possible of the data during each campaign to evaluate diurnal averages of the fluxes. We however filtered for events that could affect the quality of the concentration measured and which were untypical for that agricultural field site (rain, emission plumes), see section 3.4. Filtering for non-stationarity conditions was not necessary since we continuously sampled at two heights with two individual LOPAP instruments. Indeed any non-stationarity in concentrations was capture simultaneously at the two heights and did not affect the measured gradient, as opposed to methods based on successive sampling with a single instrument (e.g. Stella et al., 2011).

Referee #2
L166 the diurnal averaging will address precision but not accuracy – please clarify. Please give some more details of the “events” which were excluded – what proportion of the total were they, what criteria were used to identify them as abnormal.
Answer:
The errors used for the 30/5 min data (PHOTONA 1+2/3, see new Figure 3) are only precision errors, as for the calculation of the HONO flux mainly the difference between the two instruments are of importance (and not any systematic errors, e.g. any calibration error, similar valid for both instruments, calibrated by the same nitrite standard). In contrast, when the average day was formed (see data shown in Figures 4-7) the standard error was calculated (standard deviation divided by the square root of the numbers of values: $\sigma/\sqrt{n}$).
Concerning the filtering of the data, first of all only 52%, 77% and 78% of the campaign data could be used to determine HONO fluxes during PHOTONA 1, 2 and 3, respectively. For the other periods, data from all instruments were simultaneously not available (loss by calibrations, zeros, zero gradients, malfunctions etc.). From this flux data, 97%, 99%, and 57% were used to determine the average days for PHOTONA 1, 2 and 3, respectively. For PHOTONA 1 and 2 only few data were filtered caused by a rain event (PHOTONA 1: 24.08.) and by a high pollution plume (PHOTONA 2: 07.04.). In contrast, for PHOTONA 3, a significant fraction of the flux data was discarded (16.08.-21.08.) caused by low quality of the first intercalibration during this campaign, which caused untypical continuous negative HONO fluxes, which were not observed later during the campaign. For the average day we used only the data starting from the 21.08., when the next intercalibration was performed (see Fig. 2). Finally, data from the 26.08. were also not considered, caused by a strong rain event leading to negative HONO fluxes. This information will be added to the revised manuscript.

Referee #2
L190 how often were the LOPAPs intercompared – please give details. This is critical to the flux derivations / to be confident no drift in instrument response biased the results.
Answer:
During PHOTONA 1, 2 and 3 the two LOPAPs were intercompared 7, 3, and 3 times, respectively. Here, high stability of the instrument’s responses was observed during PHOTONA 1 and 2, while higher variability between both instruments was observed at the beginning of PHOTONA 3. This latter data was however not used when generating the average day (see last concern and high fraction of discarded data during this campaign). Since the small variability of the instrument’s responses is considered in the precision errors of the gradient (see equation 3), the results of the present study are not significantly biased by any instruments drifts.

Referee #2
L313 the Oswald data derived from lab experiments in which "transient" HONO fluxes were derived as soil was dried – i.e. they would have sampled an immediate response to the changing conditions, over a period of a few hours, potentially different from the field in which conditions were much more stable. Also the samples were previously dried and reconstituted (not intact cores). Does this affect the comparison / conclusion? Given the temperature link described subsequently – also a possible indicator of biotic influences?
Answer:
We agree, the experiments explained by Oswald et al. do not represent a real atmospheric situation. Thus, we already wrote in section 3.4:
"It should be stressed that in the Oswald et al. (2013) study the experimental conditions were not representative for the present field site. While in these laboratory studies the upper soil surface was flushed by completely dry air, leading to optimum HONO emissions only at very dry conditions, the relative humidity never decreased below 26 %, 31 % and 43% in PHOTONA 1, 2 and 3, respectively. More work is desirable to reconcile HONO field data with incubation experiments as performed by Oswald et al. (2013)."
However, since we do not have any other parameterization of the soil HONO source than that published by Oswald et al. we cannot comment whether any other (unknown) humidity dependence of the biogenic HONO source in a real atmosphere would affect our results. We can only conclude here that a source as explained by Oswald et al. cannot describe our field observations.
In addition also the temperature dependence of the HONO source (see Figure 6) was much weaker compared to the radiation and NO_2 dependence for each campaign (see table 1) and can be explained by any (…) heterogeneous HONO source and the expected temperature dependence of the HONO adsorption on soil surfaces. Also the temperature dependence was a much weaker influencing parameter compared to the soil humidity in Oswald et al. Here the similar HONO fluxes in both summer campaigns (PHOTONA 1 and 3) under the very different soil water contents clearly indicate that any bulk soil HONO sources (not necessarily biogenic…) cannot explain our field observations, see section 3.4.

Referee #2
L330 were any other parameters considered in the correlations – in particular aerosol loading (ideally aerosol surface area)?
Answer:
We only considered those parameters which were directly measured; see experimental section. Particle levels were not measured during the PHOTONA campaigns, since HONO formation on particles surfaces was not considered of importance (see e.g. Kleffmann et al., 2003). In addition, since all known particle sources (nitrate photolysis, NO_2+HA+hν, NO_2+SOA…) show the same HONO formation kinetics compared to similar ground surfaces in laboratory studies and since the S/V ratio of particles are orders of magnitude lower compared to the ground surfaces in near ground measurements, no significant HONO formation on particles is expected during the PHOTONA campaigns. The situation may be different at higher altitude, e.g. in the free troposphere, see the recent paper by Ye et al. (Nature, 532, 489-491, 2016).

Referee #2
L339 still not clear – a little unsatisfactory
Answer:
We agree; we could not identify a final main reason for the different results between the spring (PHOTONA 2) and the two summer campaigns (PHOTONA 1+3). That was the reason why we gave three potential explanations in lines 337-347.

Referee #2
L403 HNO_3 sometimes shows a diurnal profile with a maximum in the afternoon as inferred here, but quite different mean diurnal profiles have also been reported (e.g. Murphy et al ACP 6 5321 2006) – which would affect the nitrate photolysis conclusion here.
Answer:
We do not understand this issue, since the diurnal HNO_3 profiles shown in Figure 15c of Murphy et al. (red and black symbols) are perfectly in line with our statement showing the typical asymmetric HNO_3 profile maximizing in the afternoon. As explained in our manuscript, these profiles are a result of the main formation pathway of HNO_3 by NO_2+OH in a daytime atmosphere (especially in summer) and could not explain our HONO fluxes maximizing in the morning. If the referee considers the green data from Figure 15c of the cited paper (HNO_3 is constant over the day) heterogeneous photolysis of HNO_3 could also not explain our diurnal flux observations. Finally, we are not aware of any study in which HNO_3 levels maximized in the morning similar to our HONO fluxes.

Referee #2
L459 I wasn't quite clear how the reference RH aspect worked for the data or the fitting – please expand / clarify. May be useful to show the regression (in addition to the mean diurnal timeseries for each campaign).
Answer:
The used linear humidity dependence in equation (8) is not a results of any regression analysis, but was only added to take into consideration the positive influence of relative humidity on the proposed heterogeneous sources and sinks derived from laboratory studies at medium humidity (NO_2+surfaces/dark; NO_2+HA+hν, HONO deposition), see references in lines 458-459. The use of the 50 % RH reference humidity was accidentally chosen and any other humidity reference point could have also been used, resulting in exactly the same experiment/model agreement (after linearly adjusting the parameters A, B and $\nu(HONO)_T$). We used here 50 % RH simply because this reflects a typical average humidity in the atmosphere. In addition, a linear humidity dependency was applied here for simplicity, although laboratory derived humidity dependencies often level off at high humidity.

Referee #2
Wording
Abstract line 16 – suggest reword to "…these results are consistent with HONO formation by…"
Answer:
Changed

Referee #2
Line 38 HO_2xH_2O is not a nomenclature I am familiar with – use a period . ?
Answer:
Changed according also to the used definition of this complex in the original paper by Li et al.

Referee #2
L55-56 reword the REA phrase
Answer:
We do not understand this issue? REA is the only used abbreviation for the "relaxed eddy accumulation" method?

Referee #2
L61 an NO_2 driven mechanism
Answer:
Changed

Referee #2
L152 the abbreviations for previous decades reads a little awkwardly
Answer:
We change to: "During the 1960's and 1970's…"