Reply to Referee #2

The actual mechanism for ground/surface source of HONO is still up for debate, and high-quality flux measurements will aid in answering this question. The work by von der Heyden et al, describes an adapted LOPAP system for determining HONO fluxes by REA. In my opinion, the authors have done an good job describing the instrument, calculations and have provided a number of lab and field tests to validate the instrument for measuring fluxes. I especially appreciated how the authors listed some of the problems encountered related to flow rates and inlet pressure between the different channels and the solutions in section 3.2. It was refreshing to see, as presenting this sort of information will help other solve similar problems in the future.

We would like to thank referee #2 for her/his interest in our work and also the helpful comments, which are addressed below.

I would have liked to see more characterization or validation on the effect of having an 80cm inlet before the stripping coil on the measured HONO. HONO formation on inlet surfaces is well known, as the authors state in the text, and this inlet in my opinion reduces one of the advantages of a normal LOPAP system (i.e. the very short inlet prior to sampling). While the authors attempted to mitigate it by covering it in foil, I would have liked to have seen some experimental validation that this inlet wont lead to a bias in the measured HONO, rather than just stating that the small residence time means it won't matter.

We fully agree with the referee's concern, which we already discussed in the manuscript as a potential problem (see lines 168-172 and 327-332). However, unfortunately it is impossible for a REA-system to avoid the use of inlet surfaces, since a common inlet line, the two valves and their connections to the inlets of the two stripping coils are mandatory. In addition, caused by the dimension of the external sampling unit, there is a minimum distance to the anemometer necessary to avoid disturbances of the turbulence measurements, even if the sampling unit is placed in the lee of the anemometer. Due to these requirements we had to use a 80 cm long PFA inlet tube (4 mm i.d.) shielded against irradiation by aluminum foil to prevent for photochemical formation of HONO, e.g. by photolysis of nitrate on inlet surfaces. Since we are aware of potential inlet artefacts even in a dark inlet – that was the reason why we developed the external sampling unit for the LOPAP technique – we also increased the total inlet airflow rate to 3.7 L min^{-1} by adding the bypass flow, minimizing the gas-surface interaction time. It should be highlighted that the length of our inlet is much shorter than those used in other REA studies further minimizing the inlet artefact.

From our experience with inlet tests during the development of the LOPAP technique, artificial formation of HONO was significant when using a 3 m long heated PFA inlet line (4 mm i.d.) and a flow rate of only 1 L min^{-1}, especially at low HONO/NO_x ratios and low HONO levels during daytime. In contrast, during night-time at higher HONO/NO_x ratios and higher HONO levels, the artificial HONO formation was of less importance. However, since the gas residence time in this former inlet was almost 14 times longer than in the 80 cm short inlet used for the present REA system (see 3 m vs 0.8 m and 1 L min^{-1} vs 3.7 L min^{-1}), we do not expect significant heterogeneous HONO formation for our REA-LOPAP even at low HONO levels and low HONO/NO_x ratios. In addition, since this heterogeneous artificial HONO formation would only affect the absolute HONO levels and not the concentration differences, it would not influence the HONO fluxes. Fluxes are calculated from the concentration difference of the up- and downdrafts (see equation (1)). So even if the absolute concentrations of both air masses are

affected by significant artificial HONO formation on inlet surfaces, that would affect both air masses to the same extent and would not change the concentration differences and fluxes.

However, since we also calculate average absolute HONO concentrations using the REA data (see Figure 3), for the next field campaign, we plan to intercompare the REA-instrument with a common LOPAP, for which no inlet surfaces are used. Unfortunately, we still do not have data from such an intercomparison.

Overall, this manuscript is well written, clearly presented and will be of interest to many in the community.

We would like to thank referee #2 for this positive statement.

Minor Comments

Line 25: As you state in section 5.3, much of your discussion on potential HONO sources is speculative. I am not sure you can claim these HONO formation mechanism are minor.

We not generally claim other formation mechanism as minor, but only for the present field site. Based on the correlation of the daytime fluxes with different parameters, other formation mechanisms than the proposed photosensitized conversion of NO_2 are less likely in Melpitz, see discussion in section 5.3. With respect to a similar comment by referee #1, who suggested an alternative explanation of our results, we will also extent the discussion in section 5.3 by additional quantitative calculations. However, also these calculations show that the alternative mechanism suggested by referee #1 is of minor importance (see our reply to referee #1). We would appreciate if referee #2 has some additional suggestions how other proposed mechanisms could better explain our field data, which could be included into the discussion section.

To consider the concern of referee #2, we will weaken the sentence in line 25 by: "…, but are tentatively ranked being of minor importance for the present field campaign."

Line 140: there have been more recent instrument intercomparisons comparing HONO measurements from the LOPAP to other instruments (Crilley et al., 2019; Pinto et al., 2014), which indicate that there can be significant variability in the reported measured values of HONO between the LOPAP and other established techniques . This should be indicated here.

We are aware also of several other intercomparison campaigns (e.g. Ródenas et al., 2013), where LOPAP instruments agreed not as well to other techniques as in our cited former study Kleffmann et al. (2006). However, we consider this cited study as more relevant for the present study for the following reasons:

First, in our former study, the LOPAP was intercompared with the DOAS technique for the same air mass, since a White mirror long path absorption system collocated to the LOPAP inlet was used for the DOAS (= both instruments in-situ). Thus, we had no problems with spatial inhomogeneous air masses discussed e.g. in the study of Crilley et al., 2019 and also for some

instruments in Pinto et al., 2014 (here in-situ instruments were compared with LP-DOAS and the inlet of the LOPAP was different to the co-located inlets of the MC-IC, SC-AP and QC-TILDAS).

Second, in Kleffmann et al. (2006), neither the LOPAP nor the DOAS used any significant surfaces on which artificial HONO could be formed (long inlet lines, cavity cells, etc.), in contrast to some instruments used in the two intercomparison studies mentioned by the referee.

Third, in Kleffmann et al. (2006) our LOPAP was operated by ourselves (similar to the present REA-LOPAP) using a similar basic set-up and data treatment, which may be not the case in other studies. For example, in the FIONA intercomparison campaign (Ródenas et al., 2013), several LOPAP instruments were intercompared, some of which showing significant differences. However, reason for that, at least in part, was the individual operation of the instruments and for two LOPAPs also modifications of the original set-up. We proposed this set-up and the data treatment several years ago during the instrument's development and still use it, e.g. for the present REA-LOPAP. Generally, any instrument can produce low quality data, if not well operated. Even the DOAS instrument, which is typically defined as the "gold standard", only worked properly in the EUPHORE chamber, after a negative artefact caused by impurities of HONO in the NO_2 reference spectra was considered for (see Kleffmann et al., 2006), which is a general problem of all spectroscopic instruments working in the near UV (see also IBBCEAS).

In conclusion, by the sentence in line 140 we would like to highlight that our LOPAP instrument operated by ourselves agreed well with the DOAS technique, which might not be the case for other LOPAP instruments operated by other users for several reasons (see above). Thus, we consider the cited intercomparison as more relevant for the present study. A detailed discussion about the various intercomparisons including different LOPAP instruments is however out of the scope of the present study.

Figure 1: Why does stripping coil for channel 3 only have one coil? Wouldn't it be better if you also quantified the interferences in this coil as well?

Yes, we agree! But that was technically not possible in a standard LOPAP housing and two complete standard LOPAPs could not be integrated into the field rack, which was already quite bulky for flux measurements (see supplement Figure S5). We have discussed this issue and the validation of the applied interference correction in detail in lines 142-149, 337-346 and 427-433.

Line 311-319: I struggled to follow the explanation for the corrections applied for dilution during REA measurements. This may be better presented as equation. Furthermore, it wasn't clear to me channel 3 was treated differently to channel 1 and 2.

For both running averaging intervals (W1 and W2, see supplement Figure S3) every 30 s the PyREA software records fractions of how long each channel is sampling ambient air, which could be, for example, a third of the total averaging interval. For the other two thirds of the time, when the instrument is in the dead band, or when the other channel is sampling ambient air, zero air is sucked into the stripping coil. Thus, the measured HONO concentration reflects

a diluted sample, with a dilution ratio defined by the valve switching statistics. However, since we need the undiluted HONO concentration for the flux calculation by equation (1), the dilution was corrected for. E.g., in the example above, the measured diluted concentration would be multiplied by a factor of three. For this dilution correction, we used the shorter running average interval W1 of 5 min for the valve switching statistics, which was adjusted before the campaigns in the PyREA software to the physical time response of the LOPAP instrument. Every measured data point of the LOPAP (30 s) also reflects a 5 min running average, which is caused by the LOPAP instrument's measurement principle. For the dilution correction all channels were treated the same way. Only for channels 1+2 the valve switching statistics of valve A and for channel 3 the valve switching statistics of valve B were used (see Figure 1).

Next, the undiluted data was harmonized based on the results of the parallel ambient measurements, caused by small drifts of the instrument's sensitivity compared to the calibration results. Here again all channels were treated by the same correction. Since we do not know, which of the two channels measures correctly, we harmonized to the average of both, i.e. the smaller signal of one channel was increased and the larger signal of the other channel decreased by half of the difference of the parallel ambient measurements. Channel 2 (interferences) was harmonized in the same way than channel 1, since both channels sample the same air mass (see Figure 1). However, caused by the typical small signals in channel 2 (ca. 10 % of channel 1), any errors in the harmonization of channel 2 (typically only a 1-2 % correction), will not significantly affect the accuracy of the HONO data (i.e. by only 0.1-0.2 %, much smaller than the precision error of the instrument). Also with respect to referee #1, we will explain the harmonization in more detail in the revised manuscript (see our reply to referee #1).

After harmonization, the HONO concentrations of the up- and downdrafts were calculated in the same way as done for a normal LOPAP instrument. Here, from channels 1 and 3 (measuring HONO + interference) the signal from channel 2 (measuring only the interferences) is subtracted and the incomplete sampling of HONO in channels 1 and 3 is considered. For the correction, the signals of channels 1 and 3 are divided by the sampling efficiency of 99.6 % (see line 127) to account for the loss of HONO by incomplete sampling. In addition, the loss of HONO to the interference channel 2 (channel 1·0.4 %) is subtracted from channel 2 and only the remaining interference is subtracted from the signals in channel 1 and 3 (see lines 317-319). Also this interference correction was done in the same way in channels 1 and 3, thus we do not understand the last concern of the referee?

Finally, we agree that the data treatment is quite complex and we will try to explain that more clearly in the revised manuscript.

Line 319: what is HONO sampling efficiency of the stripping coils? I couldn't find that value in the text.

The sampling efficiency is specified in line 127 (99.6 %) and was verified by a pure HONO source. See also similar question by referee #1.

References not used in the manuscript:

Ródenas, M., Muñoz, A., Alacreu, F., Brauers, T., Dorn, H.-P., Kleffmann, J., and Bloss, W. J.: Assessment of HONO Measurements: The FIONA Campaign at EUPHORE. In: Barnes, I., Rudziński, K. (eds), Disposal of Dangerous Chemicals in Urban Areas and Mega Cities. Role of Oxides and Acids of Nitrogen in Atmospheric Chemistry. NATO Science for Peace and Security Series C: Environmental Security. Springer, Dordrecht, 45-58, doi: 10.1007/978-94-007-5034-0_4, 2013.