**Atmospheric
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Discussions

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Interactive comment on "Study of the unknown HONO daytime source at an European suburban site during the MEGAPOLI summer and winter field campaigns" *by* V. Michoud et al.

V. Michoud et al.

vincent.michoud@lisa.u-pec.fr

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First, we would like to thank the reviewers for their valuable comments on the manuscript. We answer to the comments addressed by each referee and summarize the changes made to the revised manuscript in the following document.

Response to referee #1:

>1) Treatment of the sources/sinks:
Throughout the manuscript several ground surface sources and sinks are converted

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into gas phase production and loss rates and vice versa by using the boundary layer height (e.g. in equations (1) and (2) and on page 23657, line 10-17). For these calculations, homogeneous mixing and missing gradients of HONO have to be assumed. This is however unrealistic, leading also to very unrealistic calculations. For example, on page 23657, line 10-17 a mathematical treated volume source of HONO (from the PSS) is converted into the physical-chemical correct ground source (flux density) by using the BLH. Since strong gradients are expected for a ground source caused by the short photolytic lifetime of HONO, the assumed mixing height is much too large resulting also in too large flux densities. There are now direct flux measurements during daytime available (e.g. REA measurements by Zhou et al. and Ren et al.) and they are all two orders of magnitude lower (ca. 10^{10} /cm^2/s) compared to the numbers shown in Figure 9 and 12 (right axis). The explanation for strong overestimation is the two orders of magnitude too high mixing volume for HONO, which was used here (to convert the numbers in line 17, a 1200 m BLH is necessary). Without 1-D modelling of the transport and chemical reactions of HONO (mainly photolysis) I do not recommend that kind of unrealistic calculations.

By the same argument, I also think that the deposition loss and the heterogeneous dark conversion of NO2 are underestimated in equation (2). In addition, a deposition velocity of only 0.1 cm/s (see line 7 on page 23652) may be realistic for the nighttime, but is much too low during daytime (can easily reach 1 cm/s). In contrast, for the emissions calculated in equation (2), besides a realistic estimate of the effective mixing height (source underestimated here), also the average lifetime between the emission (NOx/HONO) and the measurements site has to be considered. Since a 7x7 km NOx emission inventory was used, it is reasonable that most of the emitted HONO was already photolyzed when arriving at the measurement site (depending on wind direction, wind speed and distance of major NOx sources). Here however, the "fresh" emission ratio of 0.8 % was used. At least the high uncertainties of the used calculations should be discussed here in more detail.

The homogeneous source provided by our calculations has been tentatively turned into the form of a surface source for a better homogeneity as there is some indication (such as the better correlation when soil humidity is involved) that seems to lead us to a surface source for HONO. Nevertheless, aside this concern for consistence, we agree with the referee's point that these calculations imply a homogeneous mixing over the boundary layer which is unrealistic and leads to a too large HONO unknown flux density. Following, referee's advice these calculations have been withdrawn from the revised manuscript and only the homogeneous source formalism has been kept.

Concerning the sources and sinks calculated within the PSS2, we intended to add less known processes to the well known ones included in PSS1. The aim was to see if a rough estimation of these parameters allowed us to reconcile the calculated and the measured HONO mixing ratios. In many cases the added processes to form PSS2 are upper limits and it can be seen that none of them can reconcile PSS approach and measurement.

We hence agree that the parameterization used here for these processes are quite uncertain in the PSS2 calculations and we tried to treat this concern in the original manuscript (see on page 23651 lines 21 to 24 and on page 23652 lines 8 to 11). These high uncertainties have also been mentioned in the "Results" section of the manuscript (see on page 23655, line 22).

Concerning the use of the NOx emission inventory, it provides a surface emission factor over a grid of 7x7 km which does not mean that the emitted HONO has to travel kilometers to reach the sampling point but rather than these emissions are considered homogeneous for the pixel area. It must be clear here that, even though the measurement site was quite rural (ca. 1 km of fields all around), the sampling point was not so far from NOx emitting areas such as freeways (1.5 km south-westbound and 3 km eastbound). Then, under these conditions considering a homogeneously emitting pixel leads to an overestimation of the directly emitted HONO which helps in evidencing that the processes added to PSS1 to form PSS2 are not enough to explain the measured level.

>2) Discussion on the possible source reactions:

In the present manuscript none of the proposed HONO sources could be clearly excluded or confirmed by the measurement data (see for example end of page 23660 and top of page 23661, or top of page 23663). However, I think more meaningful conclusions could be drawn from this nice experimental study. For example, the authors showed that the day by day correlation of the unknown source with J(NO2) was much higher compared to the average correlations in Figures 11 and 14, which they could not explain. Since a photochemical ground surface source is most probably responsible for the observed high daytime HONO levels and since this source is mathematically treated as a volume source (PSS), the calculated source will certainly depend on the convective mixing of the lower boundary layer (in contrast to the true flux density of the source at the ground surface). Here, I recommend parameterization of the vertical mixing for the use in additional correlations. For example, the influence of the wind induced convective mixing can be tested by plotting the source against the product of J(NO2)x1/WS. But may be also Eddy diffusion coefficients can be estimated for the measurement height to also consider the radiative induced mixing.

For us also the fact that the day to day correlation is much better than the overall is a key observation which would deserve a greater attention if possible. We hence fully agree with the analysis of the reviewer. While they were not provided in the first version of the paper we have produced scatter plots aiming (with little success) at correlating the unknown HONO source and the J(NO2)x1/wind speed. While they show low correlation coefficient (worse than the correlation between the source and J(NO2) only), these scatter plots are now added to the supplementary material. It is hence difficult to confirm the fact that this source is a ground source.

This lack of success in indirectly correlating our observation with convective mixing emphasises the need for a more direct evaluation of the small scale dynamics of the sampled atmosphere in future campaigns aiming at elucidating the HONO source

chemical nature.

>*These correlations could confirm the proposed ground source of HONO. Since the soil source and the HNO3 photolysis may be excluded (see below) I recommend using also the NO2 concentration in these evaluations. A clear hint that NO2 may be also involved in the photochemical HONO formation is the comparison of the average formation efficiencies of HONO with J(NO2) in summer and winter shown by the slopes in figures 11 and 14. Here a factor of ca. 2.5 higher efficiency can be derived for the winter campaign, which is almost exactly similar to the ratio of the daytime NO2 levels in winter/summer (see figures 2 and 4, e.g. noon: 3.5 and 9 ppb). This observation and the excellent day to day correlation with J(NO2) (see table 3, outliers can be explained by the higher errors, see below) is in excellent agreement with the proposed HONO formation by photo-sensitized conversion of NO2 on humic acid surfaces (Stemmler et al.), which may not be visible, when only the average data is considered (see line 21-25 on page 23659).*

The point raised by the reviewer when comparing the slope of the photochemical efficiency of HONO formation and the average NO2 level is interesting and sounds convincing. Unfortunately, as stated in the original manuscript, the scatter plots between the source and the product J(NO2)*[NO2] show quite poor correlation indicating that the observed source does not involved gaseous NO2 to our point of view. These scatter plots between the source and the product J(NO2)*[NO2] are now shown in the supplementary material.

>*In contrast, since soil nitrite and nitrate were not measured and since the correlations were not improved when the NO2 data was considered, the authors tend to propose HONO formation by biological activities in the soil (Su et al.) or by photolysis of adsorbed HNO3 (Zhou et al.), see top of page 23663. However, to my opinion, both sources can be clearly excluded based on the experimental observations.*

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a) soil source:

The soil source should depend on the soil water content (SWC), for which decreasing HONO release with increasing SWC (higher solubility of HONO/nitrite) should be observed. However, from Figure 1 and 9 the highest production is observed for the highest SWC to the end of the campaign. In addition, the SWC is higher in winter compared to the summer, while the absolute sources are ca. the same (compare figures 9 and 12). In addition, this source will depend on the biological activity and the temperature of the soil, clearly making this source much stronger in summer (higher biological activity, lower Henry's law solubility) than in winter in contrast to the experimental observations (no difference in the average production in winter and summer, see Figures 9 and 12; do not consider Figures 10 and 13, see error in Figure 13, see below).

To be precise, we did not propose a soil source involving biological matter; we mentioned it as a hypothesis that cannot be excluded. The observations we have gathered (positive correlation with soil humidity and stronger source in winter than in summer could be, at first, in disagreement with an effect of the soil biological activity. Nevertheless, a closer look does not allow excluding this hypothesis. Indeed, if it is true that higher liquid content of the ground would diminish the transfer to gas phase of HONO due to its solubility, it is also true that a significant humidity is required to allow the biological activity to take place. HONO emission from this phenomenon would hence certainly exhibit a bell-shape with soil humidity (and it is not possible without additional measurement to determine where we would be on this curve). It is hence misleading to expect only negative correlation with ground humidity. Concerning the fact that temperature should strengthen biological activity, it is globally right but soil biologists report that bacterial communities can develop in a temperature range only and there have been some observations (in other environments) where the soil bacterial activity was higher at 15°C than at 25°C. We believe that such processes cannot be completely excluded and may contribute a little to the unknown HONO

source. That is why this source has been proposed as potential process involved in the diurnal HONO formation, at least for the summer campaign.

Again, one of the outcomes of our work is that future campaigns that will aim at elucidating potential ground HONO emitting processes will have to take care of the homogeneity of the surrounding ground (it was the case here) and will have to include thorough characterization of the ground physical-chemical-biological state which means involving soil biologists if the ground is natural.

>b) HNO3 photolysis:

While it is presently under discussion at which wavelength the HNO3 photolysis is active (some red-shift absorption observed in recent studies...) the process will definitely take place at lower wavelength compared the NO2+HA mechanism discussed above. Here, Stemmler et al. showed that the NO2+HA source well correlates with J(NO2), in excellent agreement with the observations of the present study, while I expect much lower correlation with short wavelengths actinic flux. Since the short wavelength J(O1D) was also directly measured, a lower correlation of a plot of the HONO source against J(O1D) compared to J(NO2) could give one indication against the HNO3 photolysis source. In addition, by comparing the source for summer and winter, for which J(O1D) will differ much more than J(NO2), could give another indication against that source. Here, the much higher source efficiency of the photochemical HONO formation (see slopes in figures 11/14) is a strong indication against the HNO3 photolysis (J(O1D) will be much lower in winter). And finally, since the photochemical activity of the atmosphere is much higher in winter than in summer (see OH levels), smaller HNO3 concentrations can be expected in winter, while the photochemical HONO source efficiency is much higher in winter than in summer. May be the authors could determine a theoretical HNO3 concentration from the OH and NO2 levels and compare correlation plots of the source against J(O1D)x[HNO3]theo and against J(NO2)x[NO2]. I am quite sure, the latter will fit better, by which again the HNO3 source could be excluded.

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In conclusion, a deeper evaluation of the experimental observations is recommended, by which more information on the potential HONO sources could be derived.

Following the reviewer's recommendation, scatter plots between the calculated additional HONO source and J(O1D) have been produced for the summer and the winter campaign and added to supplementary material. The obtained correlations are worse than correlations between the source and J(NO2) which, according to the referee, should indicate than the HNO3 photolysis can be excluded. He also suggests calculating theoretical nitric acid concentrations in addition. However, since the only loss of nitric acid is its deposition, its lifetime in the atmosphere will be too long to estimate its concentration using a photo-stationary state approximation. Thus, this calculation is not possible. The use of simulated nitric acid concentrations with the box model is not possible neither since it will depend on the methodology used for such a model (spin up method for example, see Michoud et al., 2012) and the estimated concentrations will probably not be representative of the real HNO3 concentrations.

Moreover, the referee suggests to exclude this source because smaller HNO3 concentrations are expected in winter compared to summer and similar source strengths are found between summer and winter campaigns. However, even if OH concentrations are smaller in winter (twice lower), NOx concentrations are higher and the boundary layer height is lower which could balanced the lower OH concentrations and lead to similar or even higher HNO3 concentrations in winter.

Finally, since this process involved deposited HNO3 which can accumulate over days and not gaseous HNO3, the use of gaseous HNO3 in the correlations is probably not relevant. Day to day variability of the correlations tends to indicate that a parameter characterized itself by a day to day variability is missing in it. This is also a hint in favour of a process involving reservoir species at the ground which could be deposited nitric acid or nitrate or maybe also deposited NO2 instead of gaseous NO2.

>Minor concerns:

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The following concerns are listed in the order how they appear in the manuscript.

Page 23641, line 19:
Please check the 0.25 ppb/h, see below.

The mean diurnal profile obtained for the unknown HONO source during MEGAPOLI winter campaign has been recalculated and same results have been found. Thus the mean diurnal maximum for the unknown source during this campaign is still of 0.25 ppb/h. This is further discussed below.

>*Page 23642, line 12:*
The first study in which the importance of HONO as a OH source during later daytime was identified is by Neftel et al., 1996, which should be added here.

The reference to the study by Neftel et al., 1996 has been added.

>*Page 23642, line 17:*
The references of Acker et al. 2006 and Kleffmann, 2007 are not correct here. The cited Acker et al. study is about the Hohenpeissenberg for which only a WEDD was used and also in the review by Kleffmann, 2007 no specific data on this statement is shown. Here the author may use the study by Acker et al. (2006) about a campaign in Roma and a study by Kleffmann et al. (2006) in which a DOAS was intercompared with a chemical instrument. In addition, there is still a controversial discussion on the reliability of chemical measurement techniques (see: Lu et al., 2010/factor three overestimation of a chemical instrument, Liao et al., 2006/factor of six...).

The references of Acker et al. 2006 and Kleffmann, 2007 have been replaced by the proposed references. In addition, a statement has been added to the text

to deal with the remaining controversy on the reliability of chemical measurement techniques:
"although a controversy remains on reliability of chemical measurement techniques [Liao et al., 2006]."

>*Page 23642, line 27:*
In Li et al., 2008 (NO2*+H2O), no HONO emissions were studied?

The correct reference has been added to the references list:
Li, Y. Q., Schwab, J. J., and Demerjian, K. L.: Fast time response measurements of gaseous nitrous acid using a tunable diode laser absorption spectrometer: Hono emission source from vehicle exhausts, Geophys. Res. Lett., 35, L04803, 10.1029/2007gl031218, 2008b.

>*Page 23643, line 11:*
The HO2+NO2 reaction was clearly excluded (see Tyndall et al., 1995).

A statement has been added in the text to talk about the exclusion of this formation pathway:
"Reaction between NO2 and HO2 has even been excluded by Tyndall at al. (1995)."

>*Page 23646, line 11-12:*
In Kleffmann et al. 2003, no daytime gradients were studied but strong gradients were observed during night-time. In addition the study by Sörgel et al. may not be used here, caused by the very complex conditions inside a forest canopy (different photolytic lifetimes, well separated air masses above/below the canopy...).

Both references have been withdrawn from the text.

>*Page 23648, line 8:*
Sine Afif et al. is still ("to be submitted") do not use a reference at the end, compare also page 23653, line 14).

The reference from Afif et al. is still to be submitted. Thus, it has been withdrawn from the references list at the end. Same thing has been done for Ait-Helal et al. reference.

>*Page 23648, line 24:*
"Eventually"? Should be "Finally".

Eventually has been replaced by finally in the text.

>*Page 23649, line 20:*
How is J(HONO) calculated from the Li-1800 irradiance instrument? In Michoud et al., 2012 you find "by scaling with J(NO2)". Which J(NO2), by the daytime maximum or the diurnal data? Since the diurnal behaviour of the irradiance and the actinic flux strongly depends on the wavelength and the solar zenith angle, it is not clear how an irradiance instrument can be used to calculate actinic fluxes? If the diurnal J(NO2) data is used, it would be simpler to take the parameterization of Kraus and Hofzumahaus (simple factor of ca. 5). In addition, I recommend to plot the unknown HONO source (proposed ground surface source) against the measured irradiance and not against the actinic flux (J(NO2)) (see recent study by Stutz et al.).

The J(HONO) as well as J(NO2) is measured by a spectral radiometer (LI-1800). This instrument gives the irradiance at a wavelength resolution of a nanometre from 300 nm to 800 nm. The measurement is done following the shadowed method i.e; by alternatively hiding the detector from direct solar radiation or let it measure the total solar radiation. From these series of measurements, the direct, scattered and reflected

fluxes are derived using average albedo values and the hypothesis of isotropy of the flux. These fluxes are then recombined from the calculated solar zenith angle. The total actinic flux can be derived at each wavelength from 300 nm to 800 nm (see for example Cotte et al., 1997). Then, photolysis frequencies of NO2 and HONO are calculated using quantum yield and cross section for each wavelength for these two species. Since no calibration has been made for this instrument prior to the campaign, a correction factor is applied for both photolysis frequencies using a scaling factor between J(NO2) measured by a calibrated filtroradiometer and J(NO2) measured by the non-calibrated spectroradiometer.

>*Page 23651, line 4:*
Should be "k OH+NO". The capital letter "K" is used for an equilibrium constant.

"KOH+NO" has been replaced by kOH+NO in the revised manuscript.

>*Page 23651, equation 2:*
For the uptake coefficient of NO2 on aerosols "gamma" is typically used, while the Greek n is used for a deposition velocity. In addition, it has to be explained why a 100% yield is used here (1/4...), see also page 23652, lines 13-14 (even for soot the HONO yield is often <100% and not all the particles are soot during the campaign...).

The Greek n has been replaced by a gamma in equation 2 and in the text for the uptake coefficient of NO2 in the revised manuscript. The 100% yield use corresponds to the maximum HONO formation from this source. The aim is to study the impact of this formation pathway in the conditions we encountered during the MEGAPOLI campaigns. We agree that this will lead to an upper limit of the contribution of this source to HONO concentrations calculated using equation 2 (same approach as above).

>Page 23654, lines 22-24:
However, the HONO source is also induced by the light. Thus, often the HONO/NO2 ratio shows a maximum during the daytime. A better argument may be the BLH here.

We agree with the referee and a statement has been added to the revised manuscript in consequence:

"These differences between the summer and winter can be explained by the lower photolysis frequency in winter, photolysis being the major HONO sink, as well as by a stronger temperature inversion in winter than in summer leading to a lower boundary layer height in winter."

>Page 23658, line 14:
The reaction is not important, see upper limit k published (Tyndall et al., 1995)

The NO2 + HO2 reaction has been withdrawn from the list of plausible HONO formation pathways in the revised manuscript.

>Page 23658, line 16:
Ammann

Correction has been made in the revised manuscript.

>Page 23658, line 23:
The kinetics of R3 is first order, why $NO2^2$?

Indeed the kinetics of R3 has been found to be first order and $[NO2]^2$ should not lead to an improvement of the correlation between the unknown HONO source and [NO2] alone. However, since poor correlation were found using NO2, we wanted to make sure that considering $[NO2]^2$ instead of [NO2] would not improve the corre-

lation. As it was not the case, this product has been withdrawn from the parameters confronted to the unknown HONO source in the revised manuscript, as suggested by the referee.

>*Page 23659, second paragraph:*
I recommend also to show the plots of the unknown source against J(NO2)*NO2 (at least in the supplement) also by colour code for the single days.

These figures have been added to the supplementary material.

>*Page 23660, lines 5-7:*
For the days when the PSS is equal to the measured HONO, the relative error of the unknown HONO source will be extremely high (factors...). Accordingly, I recommend weighted regression including the errors of the HONO source, which would show a very low quality of the data for these days (should not be considered too much...). Same argument for page 23662, lines 12-13.

The errors of the slopes of the correlations have been added to the table 3 and a statement has been added in the revised manuscript to deal with the poorer correlation on these days:
"On these days a high error is found on the slopes and the correlation on these days should not be considered. This can be explained by the fact that the errors of the unknown source are far larger on days where calculated and measured HONO concentrations are close since it depends on the difference of both concentrations."
Furthermore, the slopes and correlation coefficients of the weighted regression including the difference between the measured and calculated HONO concentrations have been added to the supplements.

>*Page 23661, line 18 and Fig. 9/10 and 12/13:*

The difference of the unknown source between summer and winter is smaller than a factor of three, see figures 9 and 12. In addition, I do not understand how the average day was calculated in Fig 13. When looking to Figure 12, on 9 days, the maxima are much larger than 0.2-0.25 (see Fig 13), on three day they are ca. 0.25 and only on two day the maxima are <0.2 ppb/h. Thus, the average of Figure 12 is never that data shown in Fig. 13? Compare also Fig. 11/14, same range of data... In addition, when comparing the HONO formation efficiency in Figures 11/14, there is a difference by a factor ca. 2.5 which is similar to the difference in J(NO2). Thus, the absolute source strength (ppb/h) should be ca. similar in winter and summer.

As mentioned above, the mean diurnal unknown HONO source profile calculation has been checked and similar results have been found. Indeed, cloudy conditions have been often encountered during this campaign, the maxima observed were not at the same hour each day and low sources can be found around noon even if maxima appeared higher than the campaign averaged maximum on this day. Thus, averaged missing sources are definitely not similar between summer and winter.
However, we agree that on some days of the winter campaign, the missing source strength can be as high as or even higher than the summer missing source strength, when comparing the figures 11 and 14.

>Page 23665, line 18: Möller, Plass-Dülmer

Correction has been made in the revised manuscript

>Page 23665, line 23-25: delete reference and add "to be submitted" in the text.

Correction has been made in the revised manuscript

>Page 23666, line 7: Pätz, H.-W., Schäfer

Correction has been made in the revised manuscript

>Page 23666, line 9: 108 (D21)

Correction has been made in the revised manuscript

>Page 23666, line 13: Rössler, Gäggeler

Correction has been made in the revised manuscript

>Page 23666, line 21: NO2+soot reaction...

Correction has been made in the revised manuscript

>Page 23666, line 26: Plass-Dülmer

Correction has been made in the revised manuscript

>Page 23667, line 2: Res. Chem. Intermed.

Correction has been made in the revised manuscript

>Page 23667, line 19: OH

Correction has been made in the revised manuscript

>Page 23668, line 21: Häseler

Correction has been made in the revised manuscript

>*Page 23668, line 25: Zhou, X., Deng, G., Qiao, H.*

Correction has been made in the revised manuscript

>*Page 23668, line 29: thermal reaction...nitrogen dioxide...water vapour*

Correction has been made in the revised manuscript

>*Page 23669, line 3: Gäggeler*

Correction has been made in the revised manuscript

>*Page 23669, line 13: Lörzer*

Correction has been made in the revised manuscript

>*Page 23669, line 25: Lörzer*

Correction has been made in the revised manuscript

>*Page 23670, line 1: Lörzer*

Correction has been made in the revised manuscript

>*Page 23670, line 8: Li, S.*

Correction has been made in the revised manuscript

>Page 23670, line 29: Klüpfer, Pätz, Schäffer

Correction has been made in the revised manuscript

>Page 23671, line 1: Ren, X.

Correction has been made in the revised manuscript

>Page 23671, line 2: Zhou, X., Gao, H.

Correction has been made in the revised manuscript

>Page 23671, line 4: Ren, X.

Correction has been made in the revised manuscript

>Page 23671, line 5: Zhou, X.

Correction has been made in the revised manuscript

>Page 23671, line 6: Gao, L.

Correction has been made in the revised manuscript

>Page 23671, line 24: Sörgel, Diesch, J.-M.

Correction has been made in the revised manuscript

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>Page 23671, line 28: Sörgel

Correction has been made in the revised manuscript

>Page 23672, line 4: NO3...HONO

Correction has been made in the revised manuscript

>Page 23672, line 8: 107(D22)

Correction has been made in the revised manuscript

>Page 23672, line 14: Cheng, Y.

Correction has been made in the revised manuscript

>Page 23672, line 16: 333(6049)

Correction has been made in the revised manuscript

>Page 23672, line 19: Mössner

Correction has been made in the revised manuscript

>Page 23672, line 20: ...Res., 9(special issue 4),...

Correction has been made in the revised manuscript

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>Page 23672, line 26: Rappenglück

Correction has been made in the revised manuscript

>Page 23672, line 31: Zhou, X., Gao, H.

Correction has been made in the revised manuscript

>Page 23673, line 8: Zhou, X.

Correction has been made in the revised manuscript

>Page 23673, line 12: Zhou, X., Dai, H.

Correction has been made in the revised manuscript

>Page 23673, line 13: 107(D21)

Correction has been made in the revised manuscript

>Page 23673, line 15: Zhou, X., Gao, H.

Correction has been made in the revised manuscript

>Page 23673, line 16: NOx

Correction has been made in the revised manuscript

>Page 23674, Table 1, first raw, OH data: $3x10^5$ (use point for multiplication)

Point was already used for multiplication in the first manuscript and no "$3x10^5$" was found and thus no modification has been made.

>*Page 23676, Table 3: Would be nice to use weighted regressions and include the errors of the slopes...*

No weighted regression has been used since the errors reported for parameters used in the HONO source calculations are sometimes very high and only given in percentage. Thus, the calculation of the error for the HONO source is probably overestimated and will not help here. However the errors of the slopes have been added in table 3 and a discussion about the poor correlation encountered on days where calculated and measured HONO concentrations are in agreement (see above) has been added.

Furthermore, the slopes and correlation coefficients of the weighted regression including the difference between the measured and calculated HONO concentrations have been added to the supplements.

>*Page 23677, Fig 1:*
What is soil moisture in (g/cm^2)?? Shouldn't this be the soil water content SWC in (%)? of (g/cm^3)? Why cm^2? Which column?

This is a mistake, the soil moisture is in g/cm^3 and the modification has been made in figure 1 and 3.

>*Page 23679, Fig 3:*
Dito...

See previous comment.

Response to referee #2:

>*(1) Mathematic dilemma:*
The result of this study is mainly supported by the correlation between Sunknown and J(NO2). However, Sunknown is calculated by subtracting the known HONO source from all HONO sinks which is dominated by (HONO)*JHONO, see equation 4 and figure S1.1 and S1.2. Considering the high correlation between J(HONO) and J(NO2), positive correlation between Sunknown and J(NO2) is expected mathematically. Although it is commonly accepted in the previous publications that the positive correlation between Sunknown and J(NO2) indicates a photolytic characteristic of the unknown HONO sources. I recommend that we think the positive correlation a little more conservatively without a precursor (NO2/NO3-) clearly proposed regarding this mathematic dilemma.

This issue has already been raised by Villena et al. (2011). Briefly, the Sunknown represents the missing source necessary to explain measured HONO concentrations; it counterbalances the fast HONO photolysis which is supposed to be larger than any daytime source. For example, if a non-photolytic process was involved in the missing HONO source, HONO would not accumulate as strongly as observed during daytime and a different shape in daytime HONO concentrations would have been observed. Only the diurnal variation of the source caused these observations. This remains true if the loss of HONO by photolysis is fast, which was the case during MEGAPOLI campaigns. Thus, the correlation between the unknown HONO source and J(NO2) supports a photolytic process as missing source.

>*(2) Transport and mixing:*
The wind speed from west and southwest is more than 4 m/s, see Fig 1 and Fig 3.

The transport and vertical mixing of HONO could not be neglected. Even under the assumption of well mixed air mass in both clean marine region and Paris city, wind induced vertical mixing alone could be a significant HONO sink in such high wind speed, not mention of the radiative induced mixing. Lack of vertical mixing in the PSS and Sunknown calculation can result in large uncertainty in correlation analysis. This should be considered in this manuscript at least.

The authors agree with the anonymous referee and a statement has been added in the revised manuscript to deal with uncertainties concerning the lack of vertical mixing in the PSS and the Sunknown calculations:
"In addition of uncertainties displayed before, the lack of vertical mixing in this calculation would also cause additional uncertainties."

>(3) Sunknown could be different in different air mass:
I recommend separate the days of different wind directions considering the differences in wind speed and chemical environment. As stated above, wind induced mixing could be essential as a HONO sink when west and southwest wind apply. While wind induced mixing will be smaller in case of north wind. Besides, the HONO chemistry in clean marine air mass represents an aged or a background condition while the HONO chemistry in urban air mass is similar to that of a direct emission or fresh aged mixed air mass. For instance, fresh sea salt aerosol from west may act as a sink of HONO while secondary particle from north is considered as a HONO source. By the way, the role of the total surface area of aerosol was not discussed in the result.

Concerning the impact of wind speed on the unknown HONO source, scatter plots have been made between the missing source and the product of J(NO2) and the wind speed showing no clear tendency. These scatter plots have been added to the supplementary material. Concerning the wind direction, and particularly the role of the nature of aerosol: even if wind coming from the south west sector has been called

clean oceanic air mass, the measurement site is clearly far away from the ocean (>200 km from the closest coast) and a low level of sea salt is therefore expected. Thus, only the HONO source on aerosol surface has been considered and found to be low for both campaigns (see supplementary S1).

>(4) Uncertainty in PSS2 and second thought on Sunknown calculation, see equation (1) and equation (2):
Besides vertical mixing, some parameters in this study could further contribute to the uncertainty of PSS2 and Sunknown calculation. VHONO, VNO2, Va, HONO/NOx ratio are highly variable. The choice of them is easily challenged. For instance, 0.008 are the upper limit of HONO/NOx ratio reported in the literature. It is inappropriate even for the fresh urban air mass which takes almost two hours (comparing to HONO lifetime of around 20 min.) to reach the research site according to a wind speed of 2 m/s. In addition, the assumption of no vertical gradient for HONO concentration is unrealistic and will also increase the uncertainty of PSS2 calculation. Again, in the early morning and later afternoon, the Pemission is comparable to the Punknown (see Figure S1.1 and S1.2), which means that the uncertainty of Pemission is transferrable to Punknown. At last, due to the small J(HONO) in the early morning and later afternoon, the PSS assumption is more invalid comparing to the noon time when lifetime of HONO is around 15 min, Punknown is then suffering from higher uncertainty. In all, I recommend using PSS1 instead of PSS2 to calculate Sunknown and also restrain Sunknown in the noon time in correlation analysis.

Concerning the parameterization used for HONO emission in PSS calculation, the 0.008 HONO/NOx value has been chosen because it has been determined from tunnel measurements in Germany whereas other ratios which could be found in the literature have been determined in the United States. We therefore considered this ratio for the Paris region which traffic fleet, with higher diesel engine proportion, is more similar to the German fleet than to the US one. Then, we used the NOx emission

rate from the cell of the emission inventory where the site is. In such inventory, the emission rate is considered as representative of the entire cell. Moreover, the site is surrounded by highways (between 2 and 3 kilometres away), and thus fresh emitted HONO does not take hours to reach the site. So we considered that this HONO/NOx ratio and this NOx emission rate allow us to roughly estimate fresh direct HONO emissions for our site. However, we agree that a large uncertainty is associated with this parameterization and a statement was included in the original manuscript (see on page 23651 lines 21 to 24).

Concerning the use of PSS1 instead of PSS2 for the unknown source: we used PSS2 to delete all known sources, so only the unknown processes would remain. We agree that the parameterization used for additional processes in PSS2 induces high uncertainties. We tend to calculate reasonable upper limits for the processes added to PSS1 to form PSS2. However, even in this case, they represent only a limited part of the estimated HONO concentrations. The conclusions driven in this article should hence remain the same and we therefore prefer to keep this methodology.

>*(5) Difference in correlation coefficients and slopes, see Fig14 and Table 3 under the assumption of photolytic characteristic of the unknown source, high correlation between Sunknown and J (NO2) should not fail. However, low correlation efficient is found in the days when a pretty good agreement is found between PSS and measured HONO (see line 5-8 in23660). This indicates again that uncertainty in Sunknown calculation affect correlation analysis in a bad way. Thus, both correlation coefficients and slopes need a double check with a renew Sunknown recommended above. Even though, the slopes are similar in some extent in picking days (says R2 bigger than 0.8) considering the uncertainty in calculation. The slope around 240 in the winter and 80 in the summer, however, could be a clue for HONO precursor.*

We agree with the referee that low correlation coefficients found on the days where the calculated and the measured HONO concentrations are in pretty good

agreement indicating that uncertainties on the calculated source on those days are important. A statement has been added in the revised manuscript in this sense:

"On these days a high error is found in the slopes and the correlation on these days should not be considered. This can be explained by the fact that the errors of the unknown source are far greater on days where calculated and measured HONO concentrations are close since it depends on the difference of both concentrations."

Furthermore, the errors of the slopes have been added in table 3; the slopes and correlation coefficients of the weighted regression including the difference between the measured and calculated HONO concentrations have been added to the supplements. However, correlations on these days should not be considered since no or at least very low additional source is expected these days.

Furthermore we agree with the referee that the difference in the slopes between the summer and the winter campaigns can be a clue for the identification of the process involved but with regards to the database available, no conclusion could be drawn and only supposition could be made.

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Interactive Discussion

Discussion Paper

Villena, G., Wiesen, P., Cantrell, C. A., Flocke, F., Fried, A., Hall, S. R., Hornbrook, R. S., Knapp, D., Kosciuch, E., Mauldin, R. L., McGrath, J. A., Montzka, D., Richter, D., Ullmann, K., Walega, J., Weibring, P., Weinheimer, A., Staebler, R. M., Liao, J., Huey, L. G., and Kleffmann, J.: Nitrous acid (hono) during polar spring in barrow, alaska: A net source of oh radicals?, Journal of Geophysical Research-Atmospheres, 116, D00R07, doi: 10.1029/2011jd016643, 2011

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