**Atmospheric
Chemistry
and Physics**
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.

Anonymous Referee #1

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General comments:

In the manuscript by Michoud et al. the unknown daytime source of HONO was quantified for two seasons near to Paris and possible source reactions were discussed. Since HONO is a major source of the OH radical and since formation mechanisms are still controversial discussed, detailed field studies on this topic are of high interest for the photo-chemistry of the atmosphere.

In the present study, the unknown daytime HONO source was determined including direct measurements of the OH radical levels (summer) and actinic fluxes, to correct

for known gas phase production. Thus, the daytime source is quantified only based on measured parameters, in contrast to many former studies on that topic. For the winter campaign modelling of the OH levels with the well-established MCM model was used to calculate the (unfortunately not measured) OH levels. Since the MCM often showed good agreement to OH measurements, this is also acceptable and the best what the authors could do. In the calculation of the daytime source also major known sources and sinks were considered, showing a general high quality of this study. Thus, I recommend publication in ACP after the concerns listed below are considered.

Major concerns:

1) Treatment of the sources/sinks:

Throughout the manuscript several ground surface sources and sinks are converted 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^{-1}) 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 night-time, 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.

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.

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).

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.

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 ob-

servations (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).

a) 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.

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

Minor concerns:

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

C7816

Page 23641, line 19:

Please check the 0.25 ppb/h, see 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.

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 Rom 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…).

Page 23642, line 27:

In Li et al., 2008 (NO2*+H2O), no HONO emissions were studied?

Page 23643, line 11:

The HO2+NO2 reaction was clearly excluded (see Tyndall et 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…).

Page 23648, line 8:

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

Page 23648, line 24:

"Eventually"? Should be "Finally".

Page 23649, line 20:

How is J(HONO) calculated from the Li-1800 irradiance instrument? In Michould 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.).

Page 23651, line 4:

Should be "k OH+NO". The capital letter "K" is used for an equilibrium constant.

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...).

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.

C7818

Page 23658, line 14:

The reaction is not important, see upper limit k published (Tyndall et al., 1995)

Page 23658, line 16:

Ammann

Page 23658, line 23:

The kinetics of R3 is first order, why NO2^2?

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.

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.

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

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strength (ppb/h) should be ca. similar in winter and summer.

Page 23665, line 18: Möller, Plass-Dülmer

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

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

Page 23666, line 9: 108 (D21)

Page 23666, line 13: Rössler, Gäggeler

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

Page 23666, line 26: Plass-Dülmer

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

Page 23667, line 19: OH

Page 23668, line 21: Häseler

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

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

Page 23669, line 3: Gäggeler

Page 23669, line 13: Lörzer

Page 23669, line 25: Lörzer

Page 23670, line 1: Lörzer

Page 23670, line 8: Li, S.

Page 23670, line 29: Klüpfer, Pätz, Schäffer

Page 23671, line 1: Ren, X.

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

Page 23671, line 4: Ren, X.

Page 23671, line 5: Zhou, X.

Page 23671, line 6: Gao, L.

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

Page 23671, line 28: Sörgel

Page 23672, line 4: NO3. . .HONO

Page 23672, line 8: 107(D22)

Page 23672, line 14: Cheng, Y.

Page 23672, line 16: 333(6049)

Page 23672, line 19: Mössner

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

Page 23672, line 26: Rappenglück

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

Page 23673, line 8: Zhou, X.

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

Page 23673, line 13: 107(D21)

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

Page 23673, line 16: NOx

Page 23674, Table 1, first raw, OH data: 3x10ˆ5 (use point for multiplication)

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

Page 23677, Fig 1:

What is soil moisture in (g/cm2)?? Shouldn't this be the soil water content SWC in (%)? of (g/cm3)? Why cmˆ2? Which column?

Page 23679, Fig 3:

Dito. . .

C7822