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Comment

Interactive comment on “Observations of high rates of NO₂ – HONO conversion in the nocturnal atmospheric boundary layer in Kathmandu, Nepal” by Y. Yu et al.

Anonymous Referee #1

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General comments:

In the manuscript by Yu et al. HONO, NO₂ and particles are measured in Kathmandu, Nepal for the first time and very high HONO/NO₂ ratios are observed. Some very interesting data is presented, however there are several points which should be considered before final publication in ACP. A nice part of this study is the additional measurement of the boundary layer height, which enables to determine the surface to volume ratio (S/V) of the ground, besides S/V of the particles. By this and the better correlation of the HONO/NO₂ with (S/V)ground compared to (S/V)aerosol night-time HONO formation on ground surfaces was clearly identified. This is a much better approach than

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simple correlation studies, often applied in the past.

However, besides the special comments, I have two concerns, for which the manuscript should be modified.

1) The results from chapter 3.3 in which HONO formation on soot is proposed is in contradiction with the nice correlation of HONO/NO₂ and (S/V)_{ground}. In addition, the heterogeneous HONO formation on soot particles is highly overestimated (see special comments). Besides this, the results from Fig. 5 are not very convincing, since in-situ PM₁₀ measurements are compared to space averaged long-path DOAS measurements of HONO and NO₂ (see special comments). Thus, I recommend deleting this section.

2) In chapter 3.4.2 the authors try to quantify theoretically the HONO/NO₂ ratio based on measurements of the uptake kinetics of HONO and NO₂ on aqueous surfaces. To my opinion, this is however a much too simple approach and will not work for several reasons:

a) The uptake kinetics listed (uptake and mass accommodation coefficients) refer to aqueous surfaces. However, since HONO formation on atmospheric ground surfaces may be different (most probably candidate is reaction R3 on adsorbed VOC) the uptake kinetics, for example on adsorbed organics, may be completely different for HONO and NO₂ compared to bulk aqueous surfaces.

b) The use of mass accommodation coefficients (see referred values) makes no sense for the description of heterogeneous reactions on ground surfaces (reaction of interest here, see above), since the transport (convection/diffusion) will be the limiting parameter. Thus, the use of mass accommodation coefficients will strongly overestimate uptake on ground surfaces. May be measured deposition velocities could be used for those calculations, but not accommodation coefficients.

c) The authors mixed/compared values of uptake coefficients with values of mass ac-

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accommodation coefficients, which are different processes. Even for the uptake on particles the accommodation is often not the limiting parameter. In conclusion, this part of section 3.4.2 should be deleted.

Special comments:

Page 185, R2:

This reaction was excluded in many field and lab studies and is unimportant under atmospheric conditions, which was often demonstrated by night-time HONO formation in the absence of significant NO levels. If the authors like to leave the NO reaction (NO reactions are also excluded here...), please add also the reaction of $\text{HNO}_3 + \text{NO}$, recently proposed by Finlayson-Pitt's group (could be also excluded here).

Page 185, line 14-16:

Reaction (1) has been demonstrated to be relatively slow (gamma values $< 10^{-7}$, recalculated from Finlayson-Pitts et al., 2003), and the reaction kinetics is not too much dependent on the surface properties (e.g. Teflon, glass, quartz...). Thus, formation on particles is not of importance in the boundary layer caused by the much higher S/V ratio of ground surfaces compared to particles. This reaction was already excluded for particles from field measurements and modelling (see the Vogel et al. paper and the corresponding part I paper). Simple correlation studies (for example, Notholt et al.) should not be used as reference since particles and HONO have both ground surface sources and will correlate without being chemically linked. There are many papers in which this was already clarified. For example, studies by Febo et al. show that HONO perfectly correlates with Radon (not chemically linked...).

Page 185, line 17 ff:

To my opinion, reaction 3 has not yet been demonstrated to be of importance in the atmosphere for soot surfaces (other HC(red) like adsorbed VOCs are also possible, but not discussed here). Reaction 3 is a redox-reaction with a maximum yield of ca. 10^{-14}

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HONO per cm² soot surface (the value of 10¹⁵ given on page 195 comes from unrealistic spark generator soot experiments...), which leads to insignificant atmospheric HONO formation for typical soot loading and life time in the atmosphere. (compare Arens et al., 2001, Kleffmann et al., 2005).

Page 186, line 7:

In the study of Beine et al. very low daytime HONO levels very observed (title: Surprisingly small HONO....) und thus, is not a good example here.

Page 186, line 9:

In the Arens et al. study a dark reaction was studied (no photochemistry, delete reference here...).

Page 186, line 13:

In the Bejan et al. paper, a gas phase reaction was studied (compare line 11: "...on the surface of...", thus, delete in this context...)

Page 186, reaction R4:

This type of reaction mainly takes place on ground surfaces in the boundary layer caused by the higher S/V ratio of the ground. For humic acid reaction see Stemmler et al. 2007, for TiO₂ compare S/V of dust particles to ground surfaces. Thus, generalize to: "activated surface".

Page 186, line 18 ff:

Whereas aerosol load and composition may be not too important (see above), the boundary layer height and the vertical transport are much more important parameters to understand HONO formation (please add).

Page 186, line 28 ff:

The Zhou et al. papers (2002 and 2007) are no instrument papers and the HPLC

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technique is explained in the Huang et al. paper.

Page 187, chapter 2.1:

All instruments used for the species and parameters of interest should be shortly specified. E.g. Is NO_x measured by a commercial chemiluminescence instrument with molybdenum converter? Is only the NO data taken from this instrument? How was radiation measured (see Fig. 3)? How was PM₁₀ measured ?

Since NO₂ and HONO are measured by the DOAS, which is not trivial, especially for HONO, the DOAS should be explained in more detail. For example, which cross sections were used for both species? Was the HONO impurity in the NO₂ reference spectra corrected (negative interference of the DOAS, typically 0.5 % of the NO₂)? Was a NO₂ reference measured during the campaign (in a small cell). Was this spectra used for the evaluation, to exactly match NO₂ line positions ("squeezing" and "shifting" in the DOAS evaluation...)?

Page 188, line 6:

An optical path length of ca. 2 km was used and the particle load was often extremely high (up to 1000 micro g/m³!). For such high particle load the visibility (especially in the UV) should be very short. Was there still enough light for accurate DOAS evaluation? Do the errors in the figures (Fig 3) represent the accuracy or the precision?

Page 188, line 27:

Was the I(0) at 1 m optical path length determined by the same retro-reflector than used for the long-path measurements? If not, isn I(0) different to the "true" I(0) caused by different reflectivity of the retro-reflectors?

Page 190, line 18-19 and Figure 2:

It is hard to follow a value of 100 micro m³/cm³ in Fig. 2 (scale up to 3000...). In addition, the y-axis labels in figure 2 for aerosol volume and surface should be in

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"/cm³" and not "/m³").

Page 191, line 11:

What means "frequent vehicle searches"?

Page 191, line 16:

Is there any explanation for the extreme high particle load (1000 micro g/m³...)? Seinfeld and Pandis specify <300 micro g/m³ for urban polluted conditions. Are these peaks dust events (but wind speed low...)?

Page 191, line 21-23:

The correlation of HONO with NO₂ and PM₁₀ could not only be explained by the two arguments given by the authors. An additional, more realistic explanation is that all three species have their source near the ground (not necessarily the same sources!) and should correlate, if the boundary layer height varies. Thus, although HONO is most probably formed by heterogeneous reactions on the ground, while NO₂ and PM are emitted near the ground, PM and HONO correlate without being chemically linked (see above, perfect correlation of HONO and Radon in the atmosphere...).

Page 192, line 24-26:

Higher max. HONO/NO_x ratios were often observed under polar conditions (up to 100 %) but also in the study of Zhou et al., 2007. The values given here are however the highest published DOAS values and the highest urban values.

Page 193-194, Section 3.3 and Fig. 5:

The authors tried to correlate short peaks in PM with delayed, broad increase in the HONO/NO₂ ratio and tried to explain this behaviour by heterogeneous formation on particles (s. below...). This should be done by using the simultaneous and co-located particle measurements by the DOAS, since correlation of in-situ (PM₁₀) with long-path measurements (HONO, NO₂) can lead to erroneous interpretation. For example, it

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could be also possible that the DOAS observes an increase in the HONO/NO₂ before the plume arrives to the in-situ PM monitor (depends on the wind direction, source region, sampling location etc.). I cannot see an argument why the PM plume should appear always first. If the DOAS particle data would be used, I would expect similar broad peaks in HONO/NO₂ and particles (HONO and particles will both be removed from the light path by the wind; why should HONO stay while particles move, see different time behaviour shown?)

Page 194, line 27 ff and top of next page:

The calculations given by the authors will overestimate HONO formation on soot particles, since:

- a) the max. HONO yield is only ca. 10^{14} cm^{-2} in most studies (10^{15} for spark generator soot, which is different to normal soot...).
- b) the calculations assume that all PM₁₀ is composed by soot whereas only a fraction (typically 10–30 %) will be soot (rest: re-suspended road dust, NH₄NO₃, etc.)
- c) the lifetime of soot in the atmosphere is of the order of some days, thus only a minor fraction of the soot particles are freshly emitted and only those form HONO efficiently.

In addition, the discussion given in chapter 3.4 clearly shows that HONO was formed on the ground.

Page 195, line 13–15:

The authors tried to explain HONO formation by the NO₂+soot reaction on particles in the previous section (for me still not convincing, s. above). However, the references given here refer to the reaction of NO₂+H₂O, which is mainly a ground surface source (in my opinion besides the R3 on adsorbed organics the more realistic candidate for the observed HONO formation...). Thus, either concentrate on the discussion in chapter 3.4.1 (ground source identified...) or use soot studies here for discussion.

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Page 195, lines 22-24:

The most reasonable explanation is again missing, see above.

Page 196, section 3.4.1:

This is a nice part of the study, since the boundary layer height is also measured in contrast to many other HONO studies. Thus, the much better correlation of HONO/NO₂ (NO₂ precursor of HONO) with S/V of the ground (reactive surface for conversion) compared to the S/V of particles, clearly shows that HONO formation is a ground surface process. Besides two other papers (see below) this is the most convincing study I am aware of, to demonstrate night-time formation on ground surfaces. This conclusion is however in contradiction to the previous (non-convincing...) section (formation on soot proposed). I recommend that the authors concentrate on the finding of this section. In addition at the end of this section the authors should add the references of Vogel et al., 2003 and Kleffmann et al., 2003 (part I+II), since these studies better demonstrate that formation on particles can be excluded compared to the listed references (gradient of HONO, NO₂ and particles are measured there for the first time). In contrast, gradient studies of only HONO and NO₂ (cited studies) cannot exclude formation on particles (for discussion see: Kleffmann et al., 2003).

Page 197, line 9-11:

The high correlation of HONO/NO₂ with RH is not a proof for the humidity dependence of the night-time HONO formation. HONO/NO₂ is increasing during the night caused by heterogeneous formation (see above) and a decreasing boundary layer height. In addition, during the night RH is increasing caused by the decreasing temperature. Thus, a correlation of HONO/NO₂ and RH is clearly to be expected, without a necessary chemical link between humidity and the chemical process of formation. This should be discussed. If the authors want to proof the humidity dependence of the formation process they should plot the individual heterogeneous rate constants of formation of HONO by NO₂ conversion (from the increasing HONO/NO₂ ratio for each night, for

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details see Alicke et al., 2002) against the individual average humidity of each night.

Page 197, line 12ff:

In contrast, the explanation of the decreasing HONO/NO₂ at RH >96% by uptake on an aqueous film on ground surfaces is quite convincing and nicely done.

Page 197, line 19 ff and page 198:

Delete or completely modify this section, see above.

Page 199, second paragraph:

In this paragraph, the authors try to explain the decreasing HONO/NO₂ at high humidity by uptake on growing particles. However, since they have demonstrated that HONO is formed on ground surfaces (see above), also the uptake on growing water films is expected to be more important on the ground (the S/V and the amount of water taken up by particles compared to the ground should be discussed, which should be higher for the ground...).

Page 200, lines 2-4:

Please add recent dew studies from Rubio et al.

Page 200, lines 4-6:

How should an increasing particle diameter reduce the conversion efficiency? Heterogeneous HONO formation is correlated to the S/V and by particle grow the S/V should increase. However, particles should be of lower importance at all (see above).

Page 200, section 3.4.3:

The discussion about the water uptake on surfaces, the mass accommodation coefficient of HONO and the solubility of HONO as a function of temperature is either not of importance (accommodation) and completely unknown (solubility, water uptake) for these measurements. Since uptake of HONO on ground surfaces is not limited by the

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accommodation, but by diffusion (see above) any discussion about the accommodation makes no sense. In addition, even if the amount of water on surfaces could be determined anyhow, the pH of the film is the most important parameter for the effective solubility of HONO (the effective Henry's law constant is changing by some orders of magnitude for atmospheric relevant pH range...). Thus, discussion about changes in water uptake (type II or III) and the accommodation coefficient by small factors is not of importance here, unless the pH is known (was not measured here...). Thus, I recommend deleting also this paragraph.

Page 202, line 10 ff:

Besides the NO₂ hydrolysis, (R2), the dark reaction (R3) on adsorbed organics (not soot as referred here...) recently proposed by several studies (for example: Arens et al., 2002) should be also considered. It is much faster than (R2) at atmospheric NO₂ levels (gammas 10⁻⁵ - 10⁻⁶ compared to 10⁻⁷ - 10⁻⁸ for R2) and the observed first order dependence in NO₂ can be explained much easier. For this mechanism N₂O₄ and any discussion about the temperature dependence of the equilibrium is not necessary.

Page 202, lines 19-20:

I do not understand this sentence, since HONO was measured several times in South Asia (compare Tab. 2...).

Page 202, lines 21-22:

Change, see above

Page 202, lines 23-24:

Change, see above

Technical corrections:

Page 186, line 11: Should be: TiO₂...

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Page 198, line 16: The reference by Msibi et al. is not the correct one (N2O5...), it should be their 1993 paper...

Page 202, line 13: should be "dimer"

Page 203 ff, references:

Page 203, line 17: Möller

Page 203, line 20: Möller

Page 204, line 9: Rössler, Gäggeler

Page 204, line 12: Andrés-Hernández

Page 204, line 17: Gäggeler

Page 204, line 19: Gäggeler

Page 204, line 24: Abbatt, J. P.:

Page 204, line 29: Dominé

Page 205, line 3: Schurath, Ponche

Page 207, line 4: Zhou, X., Gao, H.

Page 207, line 13: Zhou, F., Shao, K., Zhang, Y., Tang, X.

Page 207, line 16: Zhou, X., Deng, G., Qiao, H.

Page 208, line 9: J. Chem. Soc. Faraday Trans.

Page 208, line 20: Lörzer

Page 209, line 23: nitrogen dioxide nitrous acid

Page 210, line 7: field measurements

Page 210, line 17: nitrous acid ... optical absorption

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Page 211, line 5: Brüning

Page 211, line 27: Müller , Brüggemann

Page 212, line 7: Wang, S.,

Page 212, line 31-32: "Vecera" with special "c" and "r" (I cannot edit...), nitrous acid....
nitrous acid

Page 213, line 3: Wang, S.

Page 213, line 27: Zhou, X.,

Page 213, line 30: Zhou, X.,

Page 215, Table 2:

This is a good idea to summarize existing HONO field campaigns in Asia. However,
some studies are missing either in the table or at all:

Takenaka et al., Analyst, 2004

Hao et al., J. Environ. Sci., 2006

Lin et al., Atmos Environ. 2006

Shou et al., J. Atmos. Chem. 2007

Su et al., J. Geophys. Res. 2008

Su et al., Atmos. Environ. 2008

Page 218, Fig.3:

Unit of radiation $W\ m^{-2}$

unify units either with brackets (%) or without

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 183, 2009.

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