**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "Observations of high rates of NO$_2$ – HONO conversion in the nocturnal atmospheric boundary layer in Kathmandu, Nepal" *by* Y. Yu et al.

Y. Yu et al.

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We appreciate the referee's detailed comments, suggestions, and technical corrections. Here are our responses to referee's commnets.

Comment 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.

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Response 1) There is no evidence contradicting sections 3.3 and section 3.4 in our opinion. Section 3.3 showed ADDITIONAL HONO formation through a plume event. However, as we mentioned in the paper, these events are short lived (usually several minutes) and the contribution of HONO formation from such plume events to total nocturnal atmospheric HONO formation is limited.

Comment 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 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.

Response 2) We partly agree with the referee's suggestion. Uptake rate coefficients used here are from published laboratory research data. The hypothesis suggested by the referee of VOC reaction with NO2 is dependent on the adsorbed VOCs on the ground surface or other surface. There is no published data from field observations, which provide such VOC data. Arens et al. 2002 and Gutzwiller et al. 2002 had published papers studying the reaction of VOCs with NO2 to form HONO. As the referee

suggests, the VOCs on the surface are the major source of HONO in the Kathmandu atmosphere. Here we made a simple calculation based on a published VOC reaction pathway with NO2. Assuming each loss of NO2 (gas phase) will form one HONO, and then equation (2) in Gutzwiller's paper (formation of HONO) should be:

d[HONO]/dt = d[NO2(gas)]/dt = Gamma(VOC+NO2) *c(NO2)/4*(S/V)*NO2(gas);

And loss of HONO:

d[HONO]/dt = Gamma(HONO) *c(HONO)/4*(S/V)*HONO(gas);

When [HONO] reaches the pseudo steady state (PSS), the ratio of [HONO] to [NO2] is determined by the following equation (similar to equation (5)-(6) in our paper):

[HONO]/[NO2] (PSS) = Gamma(VOC+NO2)/ Gamma(HONO);

The values of reaction probability (Gamma) are around 10-5 with high concentration (1M) of reactants (VOCs). Those values of Gamma are lower with lower concentration of reactants. The loss of HONO reaction probability on the surface water is in the range of 10-4 -10-2. If the VOC reaction with NO2 is a major source of HONO, we should expect a maximum of around 0.1 of values of [HONO] to [NO2] with a high concentration of adsorbed VOCs on the surface. Evidently, our observed values of [HONO] to [NO2] are much higher than 0.1. However, the calculation in our paper based on the published data (which also assumes that each NO2 lost results in the formation of one HONO), gives much better estimates of HONO-NO2 ratios. The mechanism of HONO formation is still not clear so far. It is better to wait for more field observations / laboratory studies to be done and leave the questions open than hastily drawing a conclusion. The part of the calculation that used mass accommodation coefficients has been removed from the revised paper. We kept the calculation using the uptake coefficients.

Special comments: Page 185, R2: This reaction was excluded in many field and lab studies and is unimportant under atmospheric conditions, which was often demon-

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strated 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 HNO3+NO, recently proposed by Finlayson-Pitt8217;s group (could be also excluded here).

We agree with the referee's suggestions. Actually, we had concluded in section 3.4 of the paper that NO is not an important source for HONO formation in the Kathmandu atmosphere. We will describe the R2 as possible source (not important) and add the NO2 reaction with VOCs on the surface in the revised paper.

Page 185, line 14-16: Reaction (1) has been demonstrated to be relatively slow (gamma values <10710;-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 liked...).

Laboratory research of NO2 hydrolysis used high NO2 concentrations (i.e. Finlayson-Pitts et al., 2003). Gamma values obtained from such high NO2 experiments are usually lower than low NO2 experiments, due to surface saturation. It is true that the HONO formation through particles is not important when there is the low S/V ratio of aerosol compared to active ground surface. However, in the Kathmandu atmosphere, there is extremely high aerosol loading, and it is quite likely that the aerosol composition is different from that found in European cities as mentioned in our paper and by referee 2. The mechanism of HONO formation is complicated. It might be different due to

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various conditions, which is a major motivating factor for conducting HONO research at different sites outside of North American and European cities.

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} HONO per cm^{2} soot surface (the value of 10^{15} 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).

Yes. The formation of HONO through the NO2 reaction on the soot might not be a major source. According to the discussion by Aubin and Abbatt (2007), only certain specific conditions of high NO2 concentrations and high and fresh soot loadings with large surface areas will contribute significantly to production of evaluated HONO in the atmosphere. However, the reaction of NO2 on the soot surface still is a source of HONO production especially under conditions of high NO2 and high soot loading.

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.

We accepted the referee's suggestion. The reference of Beine et al. 2006 is deleted in the revised paper.

Page 186, line 9: In the Arens et al. study a dark reaction was studied (no photochemistry, delete reference here...).

We accepted the referee's suggestion. The reference of Arens et al. 2002 is deleted in the revised paper.

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...)

We accepted the referee's suggestion. The reference of Bejan et al. 2006 is deleted in

the revised paper.

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).

We partly agree with the referee's opinion. It depends on the conditions; the ground surface is an important source of HONO, but active aerosol with similar S/V as active ground might be important too. Many laboratory studies use very high concentrations of aerosol, and thus might not be relevant in certain atmospheric conditions (such as those found in European cities). However, recent observation of high HONO in Asia (for example, in Chinese cities, see references in Table 2) indicated the influence of high aerosol loadings to HONO formation. We added "the boundary layer height and the vertical transport" in our revised paper.

Page 186, line 28 ff: The Zhou et al. papers (2002 and 2007) are no instrument papers and the HPLC technique is explained in the Huang et al. paper.

We accepted referee's suggestion. The references of Zhou et al 2002 and 2007 are deleted in the revised paper.

Page 187, chapter 2.1: All instruments used for the species and parameters of interest should be shortly specified. E.g. Is NOx measured by a commercial chemilumines-cence 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 sec-tions were used for both species? Was the HONO impurity in the NO2 reference spec-

tra corrected (negative interference of the DOAS, typically 0.5DOAS evaluation...)?

The details of DOAS instruments and other instruments have been presented in our former papers [Yu et al., 2004 and Yu et al., 2008 a]. We have added information about the manufacturers of the NOx, O3, PM10, weather station in the revised paper.

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/m710;3!). 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?

As we described in the paper, some DOAS data loss were occurred due to heavy fog and smog every morning and some evenings. Extremely high aerosol or water droplet loading will totally block the light and there were no DOAS measurements during such periods. Besides such heavy fog and smog conditions, there is enough light for accurate DOAS evaluation. The errors in the figures (figure 3) represent the accuracy of data.

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?

Yes. It was determined by the same retro-reflector. We stored the I(0) spectra in computer before we set up the 1km retro-reflector. For more details about I(0), see the references of Notholt et al, 1991 ,1992a and Notholt and Raes, 1990.

Page 190, line 18-19 and Figure 2: It is hard to follow a value of 100 micro m710;3/cm710;3 in Fig. 2 (scale up to 3000...). In addition, the y-axis labels in figure 2 for aerosol volume and surface should be in "/cm710;3" and not "/m710;3").

Yes. We changed the units in the revised paper.

Page 191, line 11: What means "frequent vehicle searches"?

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We carried out our field campaign at a time of "curfew".

Page 191, line 16: Is there any explanation for the extreme high particle load (1000 micro g/m710;3...)? Seinfeld and Pandis specify <300 micro g/m710;3 for urban polluted conditions. Are these peaks dust events (but wind speed low...)?

Kathmandu has much higher PM concentrations than the "typical" urban area described by Seinfeld and Pandis. There are several contributors to Kathmandu8217;s very high PM in the mornings and some evenings: the stable and low boundary layer, emissions from house cooking and heating, traffic emissions, low wind speed, and very high relative humidity. For More details, please see references of Sharma et al., 2002; Sharma, 1997;Yu et al., 2007;Giri et al., 2006; Kondo et al., 2002;Regmi et al., 2003;Panday, 2006.

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 there 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...).

Yes. We agree with referee's suggestion. We have added the additional explanation in the revised paper.

Page 192, line 24-26: Higher max. HONO/NOx ratios were often observed under polar conditions (up to 100

Yes. We agree with referee. We changed the wording in the revised paper.

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

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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 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?)

The time resolutions of instruments (DOAS, NO and PM10) are different. The DOAS had a time resolution of 5-10 minutes, while the NO and PM10 monitor had a time resolution of 10 seconds. We synchronized the instrument clocks before the field campaign to minimize the time difference between the three instruments. The light attenuation didn't show similar broad peaks in HONO/NO2 and particles as the referee expected. Other research (Wang et al. 2003) had observed a similar response in Texas, USA. Wang et al. (2003) observed enhanced HONO formation after a dust plume. We still believe our observation is real and valuable to HONO heterogeneous formation.

Page 194, line27 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 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.

a) We used the average value of several published HONO yields. b) We discussed in Section 2, that the PM1 to PM10 ratio is around 0.5. The aerosol surface area is

provided mostly by fine particles, which might be a minor mass contribution to the total aerosol mass. c) We agree with the referee. As we showed in chapter 3.4, the major source of HONO formation is from the ground. However, we discussed ADDITIONAL HONO formation in this section (which may be small compared to other sources of HONO). The de-active soot doesn't have any contribution to HONO formation. Our observation of ADDITONAL HONO formation after plume spike actually only occurred during a short interval. We don't see any contradiction between your opinion and our data.

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.

We have added the estimation of HONO production after the plume spike in the revised paper, which is a relatively small contribution. In chapter 3.4, we focused on the contribution to HONO formation from ground or aerosol surfaces. We concluded that there is the better correlation of ground surface with HONO formation.

Page 195, lines 22-24: The most reasonable explanation is again missing, see above.

We added the referee's suggestion in revised paper.

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).

We appreciate referee's comments.

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

It is true that the increasing of RH at night is a common phenomenon, however, it8217;s too early to say that it is common for [HONO]/[NO2] to increase with increasing RH in urban or remote atmospheres at night. In our observation, the value of [HONO] /[NO2] was not always increasing at night in the paper. As we mentioned in the beginning of section 3.4.2, the laboratory research showed the RH dependent HONO formation. The reason of RH dependent HONO formation might be due to water uptake on the surface, which was studied in pervious laboratory researches. We had discussed the

water uptake and temperature influence in section 3.4.2 and 3.4.3. Furthermore, the discussion (Page 17, line 19 ff and Page 18) described the theoretical possibility of RH dependent HONO formation. However the conditions (temperature, RH, wind, and other parameters) in real atmospheric observations are more complicated than in laboratory research. The RH dependent HONO might not be so straightforward.

Page 197, line 12ff: In contrast, the explanation of the decreasing HONO/NO2 at RH >96Page 197, line 19 ff and page 198: Delete or completely modify this section, see above.

We think it is necessary to keep this paragraph (see above), however we deleted the mass accommodation coefficient calculations.

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...).

There is a misunderstanding. We try to explain that the water uptake happened on the surface of particles, and it should be applied to ground surface (see the next paragraph).

Page 200, lines 2-4: Please add recent dew studies from Rubio et al.

Added.

Page 200, lines 4-6: How should an increasing particle diameter reduce the conversion efficiency? Heterogeneous HONO formation is correlated to the and by particle grow the S/V should increase. However, particles should be of lower importance at all (see above).

In general, increasing particle diameter reduces the conversion efficiency. Figure 6

showed increased total S/V (due to S/Vaerosol increase). However the HONO formation didn8217;t increase, which indicates the lower importance of particles as the referee suggests.

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 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 Henry8217;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.

We deleted the water uptake paragraph, kept the solubility part and added reefer8217;s comment of pH in the revised paper.

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 10710;-5 - 10710;-6 compared to 10710;-7 - 10710;-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.

The mechanism of N2O4 hydrolysis is still widely used in laboratory research and also often extrapolated to real atmospheric conditions laboratory research papers that discuss atmospheric implications. It is necessary to indicate the unimportance here.

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We added the referee's suggestions in the revised paper.

Page 202, lines 19-20: I do not understand this sentence, since HONO was measured several times in South Asia (compare Tab. 2...).

South Asia (South Asia typically consists of Bangladesh, the British Indian Ocean Territories, Bhutan, India, the Maldives, Nepal, Pakistan and Sri Lanka. Some definitions may also include Afghanistan, Myanmar, Tibet, and Iran) and East Asia (East Asia typically consists of China, Japan, Korea, Mongolia) are different geographical concepts.

Page 202, lines 21-22: Change, see above Page 202, lines 23-24: Change, see above

We appreciate the referee8217;s detailed technical corrections. We made the changes in the revised paper.

Technical corrections: Page 186, line 11: Should be: TiO2... S19 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 S20 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.

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2007 Su et al., J. Geophys. Res. 2008 Su et al., Atmos. Environ. 2008

Page 218, Fig.3: Unit of radiation W m710;-2 unify units either with brackets (

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