

Interactive comment on “Daytime HONO Vertical Gradients during SHARP 2009 in Houston, TX” by K. W. Wong et al.

Anonymous Referee #2

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The authors present daytime vertical gradients of HONO and NO₂ measured over Houston (TX) during the “SHARP” campaign by Differential Optical Absorption Spectroscopy (DOAS). In situ measurements of J(HONO), NO and OH were taken to calculate a steady state for gas phase HONO formation, to infer a daytime source of HONO. This unknown source normalized to NO₂ values correlates better with solar irradiance than with actinic flux, which the authors take as an argument for a ground source (most probably conversion of NO₂ on the ground). Although HONO forms clear gradients, the parallel NO₂ gradients made interpretation difficult. The authors therefore provide several lines of arguments to compare possible formation of HONO on aerosol and the ground surface. Whether HONO is generated predominantly at the ground or aerosol surface is important information for understanding tropospheric chemistry of HONO. The paper is generally well written and provides new interesting data on day-

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time HONO chemistry. Therefore, I support publication of this manuscript in ACP after addressing the following comments:

General comment on “photolysis”: The usage of the term “photolysis” is sometimes confusing. The formation of NO₂^{*} is a photo excitation (beyond the dissociation threshold) as, photolysis by definition implies a breakup of the molecule (e.g. P24366 and P24384). Although the authors use consistently photolysis frequency for J(HONO) throughout the text, on page 24367 it is called photolysis rate. If you like to use another term, this would be the photolysis rate constant as the photolysis rate would be J(HONO)×[HONO]. Furthermore, on P24369 the HONO yield depends on NO₂ photolysis frequency not on NO₂ photolysis (this may refer to more passages in the text). On the same page the humic acids are not photolyzed. They absorb light (photo excitation) and then transfer this gained energy to another molecule (so called “photosensitized reaction”).

P24368, L 6-21: As this paragraph is a summary of the last 30 years of research on atmospheric HONO the cited references are only a selection. You may indicate that by “e.g.” in front of the citations. L 24: Ziemba et al. (2010) find no light-dependence of their proposed reaction (see also below comment).

P24370, L21: As the proposed heterogeneous source is not light dependent (Ziemba et al., 2010), I suggest deleting or moving this citation. What is the influence of such a non-light-dependent reaction at the aerosol surface on your vertical profiles?

P24371, L21: Kleffmann et al. (2003) did not measure gradients during daytime. All discussed gradient measurements in this publication refer to nighttime. During daytime these authors measured at constant altitude (30m). But I am aware of two other publications (Häseler et al., 2009, Sörgel et al., 2011) about daytime HONO vertical distribution.

P24372, L25: Please explain what “UCLA” means. Presumably: University of California Los Angeles.

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P24374, L7: How were these concentrations scaled?

P24374/75: 2.2 radiation measurements: In their later analysis the authors discuss correlations of the HONO source to actinic flux and solar irradiance in the visible and the UV. As the instrument to measure solar (visible) irradiance is only sensitive to wavelength from 400-700nm I assume that UV-irradiance (290 – 385 nm) was retrieved from the spectroradiometer (SAFS). Although, possibly contained in the cited literature, it would be nice to add a sentence about how actinic flux and irradiance values were retrieved from the same instrument. As the differences in both are essential parts of the discussion. Furthermore, where was the optical collector of the SAFS mounted? This may be critical as the reflected radiation (large part of the difference between irradiance and actinic flux) might be very heterogeneous in the urban canopy. So my question is, are the actinic flux values only representative for moody tower or do they reflect an averaged scenario. In a more general way, what is the influence of the rough urban canopy (shading patterns, street canyons) on the difference of irradiance and actinic flux?

P24377, L 7: “Elevated daytime HONO mixing ratios”. Elevated with respect to what?

P24378, L16: In contrast to the presented data, these observations were made in rural environments (Zhou et al., 2001 even in the arctic). Measurements in urban areas showed a diurnal cycle similar to your observations, as stated in your conclusions.

P24379, L4-6: This implies that HONO formation at that time of the day could be well explained by gas phase chemistry only, as also suggested by Fig. 5. As from Fig. 3 I would suggest 7:00 CST being shortly after sunrise one would still expect “excess HONO” from the nighttime accumulation leading to higher observed HONO/NO₂ ratios. Do the authors have any explanation for that? For example, is the HONO/NO₂ ratio lower due to traffic emissions in the early morning (Fig. 3 and Fig. 5)?

L15: Any explanation for the jump in boundary layer height in the late afternoon (Fig.4a). Does this have an observable influence on the vertical gradients?

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P24380, L15: This should be 18th May instead of 19th.

P24382, L13-19: The NO₂ scaling approach is similar to that of Sörgel et al (2011) for a semi-rural environment.

P24383: 4.2 Possible daytime HONO formation pathways: A new possible source was published after this manuscript (Su et al., 2011). Can the authors comment on the possible influence of soil produced HONO in the urban area of Houston.

L 17: I'm curious to know, how the 5 min vertical transport timescale was estimated.

P24384, L 20: This has also been shown by a very recent kinetic study (Amedro et al., 2011; published after this manuscript).

P24387, L 3: Given that the differences in the correlation coefficients between P_{norm} and ultraviolet respectively visible irradiance are significant, how does this compare to the mechanism of Stemmler et al. (2006) which also works for the visible region (400-700nm).

P24387, L16: It would be less confusing using consistently “solar irradiance” instead of alternating between “solar irradiance” and “solar radiation” especially as your measurements of solar irradiance only reflect a part of the solar radiation. This also applies to Figs. 8, 9 and 10 where the axis titles are “solar visible radiation”, “solar radiation” and “solar visible irradiance”. Do they all mean the same?

P24390, L13: Kleffmann et al. (2003) did not measure daytime gradients (see above comment). Thus I suggest deleting this reference.

P24403/4, Figure 3 and Figure 4: If possible avoid overlapping of numbers. In the text and the axis title J(HONO) is used as proxy for actinic flux, whereas in the figure caption J(NO₂) is given as measured quantity. Please clarify. If possible use different symbols (dots, triangles, . . .) for the different heights and explain them in the figure caption.

Technical: P 24373, L28: (“ . . . path-integrated mixing”) ratios. . . P 24383, L10: 300_m

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References:

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