

Interactive comment on “Modeling of daytime HONO vertical gradients during SHARP 2009” by K. W. Wong et al.

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Response to Reviewer #1

We would like to thank the reviewer for the helpful comments. Please find our responses in italic in the following.

P27779 L3 et seqq.: Kleffmann et al. (2003) did not measure daytime profiles. Sörgel et al. (2011) did observe gradients, but they were overcome by extensive vertical mixing (by coherent structures) around noon. Häselser et al. (2008) report negative gradients for the autumn campaign, but were not able to detect gradients in July (convective BL?). As the profiles reported by Zhang et al. (2009) were also influenced by atmospheric stability these studies (Häselser et al., 2009; Zhang et al., C12971

2009) should be also included in the discussion on modeled vertical profiles.

Response: We used Kleffmann et al. (2003) as the reference because daytime vertical profiles were measured in a similar setup by the same group at that time. However, we agree with the reviewer that Kleffmann et al. (2003) do not clearly address daytime profiles. The reference has thus been changed to Kleffmann 2007, which mentions the daytime results from the study described in Kleffmann et al. (2003).

Häselser et al. 2009 concluded that HONO mixing ratios were independent of altitude.

We have included the results of Zhang et al. (2009) and Häselser et al. (2009) in the conclusion. The sentences “Zhang et al. (2009) and Häselser et al. (2009) suggested that vertical mixing has a large impact on daytime HONO vertical gradients due to the observation of weakening HONO vertical profiles in convective boundary layers. However, no further investigations on vertical mixing have been carried out in these studies.” have been added before “Our model also shows that vertical transport plays a crucial role in distributing HONO from its surface source(s) to the entire boundary layer. 56–59 % of the HONO loss in the lowest 20 m of the atmosphere is due to upward transport, 25 % by deposition, and only 16–18 % due to photolysis.”

P27782 L22: If heterogeneous reactions are considered, the reactive surface area available is important. How do the authors account for this? I found a statement in the conclusions (P27800 L7-L14) “...the true atmospheric surface area available for chemistry is likely one or two orders of magnitude larger than the geometric surface area used in the model, and thus the uptake coefficient is of the correct magnitude...”. Maybe this important issue should be discussed prior to the conclusions.

Response: Observed aerosol surface area is used in the model for reactive sur-

face area. In addition, the ground surface is assumed to be flat. No buildings or trees are considered. The parameterization of the formation and loss of HONO on surfaces have been described in the sections 2.2 Model Description and 2.2.1 Parameterization of HONO Chemistry.

We agree with the reviewer that we should comment on the large reactive uptake coefficient used in the model prior to the conclusions. Therefore, in Section 3.2, after the sentence "The maximum reactive $\text{NO}_2 \rightarrow \text{HONO}$ uptake coefficient that best explained our observations was found to be 6×10^{-5} , which is larger than, but of the same order of magnitude as, the laboratory values reported by Stemmler et al. (2006).", the following sentence has been added "One possible reason for the large uptake coefficient used in the model is that the model assumes a flat ground surface, while true surfaces have larger effective surface areas."

P22789 L21: "...followed by it gas-phase..." =>followed by the gas-phase...

Response: Correction has made (page number should be P27798)

P27792 L26: It should be clear that even with the rate constant given by Lee et al. (2008) the model underestimated the HONO values and that the cited studies (Carr et al. 2009; and Amedro et al., 2011) confirmed a rate constant about an order of magnitude lower, which was proposed by the original work of Crowley and Carl (1997). Please clarify.

Response: To clarify this, in the same section (P27792 L26), the sentence "The gas-phase mechanism through NO_2 is too slow to reproduce the observed daytime HONO mixing ratios, confirming other studies that found this mechanisms to be unimportant (Carr et al., 2009; Amedro et al., 2011)." is modified to "Even with the rate constant suggested by Li et al. (2008), the gas-phase mechanism through NO_2 is

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too slow to reproduce the observed daytime HONO mixing ratios. This confirms other studies that found this mechanism to be unimportant (Carr et al., 2009; Amedro et al., 2011)."

P27796 L6: Fig.8 or Fig.9?

Response: It should be Figure 9. Correction has been made.

P27796 L17 and Fig. 9: I suggest that only the important processes should appear in Fig.9., as most terms in the figure legend, like Pground; P ground photolytic, P aerosol, E (Emission), L ground, L aerosol, do not appear in Fig.9 or are invisible as they fall on one line at the bottom. Furthermore, $d[\text{HONO}]/dt$ and $\text{LHONO}+\text{OH}$ fall on one vertical line (close to zero). The figure might be improved by using thinner lines and a log profile for the height, or by only showing Lphotolysis, $\text{PNO}+\text{OH}$, Paerosol and the vertical transport term. Furthermore, it should be mentioned in the figure caption that the vertical transport term combines all surface processes.

Response: We have considered the reviewer's comment. However, this will make the legends and/or scales of Figure 9 and Figure 10 inconsistent. We are afraid that the proposed change would confuse the reader. Therefore, we decided to keep Figure 9 as it is.

We are not clear what the reviewer means with "the vertical transport term combines all surface processes" We therefore added the following sentence to the caption to clarify the meaning of this term "The vertical transport term describes how much HONO is added or removed by vertical transport at each altitude."

P27817 (Fig.8): It would be useful to have the information about the model run "photo-lytic ground and aerosol source" also in the figure caption (not only in the text).

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*Response: The following sentence has been added to the caption of Fig. 8:
"Results are from model runs with photolytic HONO sources at the ground and on
aerosol."*

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