Responses to the comments of anonymous referee #1

Thank you for your comments. Please find below your comments in blue, our responses in black and modifications in the revised manuscript in *italic*.

Additional comments from reviewer 1:

First, one needs to make sure that one does not get the wrong impression of the importance of daytime vs. nighttime formation of nitric acid leading to aerosol nitrate formation. Doing an eye-ball integration under the curve in figure 5b (now 6b) leads to an estimated HNO3 of about 0.6ppb (or about 1.5 ug m-3). Doing the same for 6c leads to about 0.18 ppb (they might want to do this more precisely). Further, they need to provide further support for their statement "Although most of the HNO3 comes from the daytime reaction of OH with NO2, since the deposition rate of HNO3 is very high, the main pathway leading to the formation of PNO3 is the hydrolysis of N2O5 at night, when the temperature is sufficiently low for partitioning to the particle phase." They could do this by switching of the N2O5 hydrolysis route, or, better yet, have the product of that reaction to be a marked HNO3.

First of all, there was probably a misunderstanding about the figures: The Figs. 6b and 6c in the revised version are not the same as Figs. 5b and 5c in the previous version of the manuscript. The previous Fig. 5b (daytime HNO_3 production) and Fig. 5c (nighttime HNO_3 production) are Fig. 6a and Fig. 6b, respectively, in the revised manuscript.

We agree completely with the referee that the daytime production of HNO_3 is higher than the nighttime production and we have emphasized it in the revised manuscript. The diurnal cycles of HNO_3 concentrations usually show a distinct minimum during early morning hours and a maximum in the afternoon with a rapid drop near sunset (Fischer et al., 2006; Aas et al., 2012). The modeled diurnal cycle of HNO_3 in this study shows a similar behavior with concentrations in the evening lower than the increase in nitrate concentrations at night (see Fig.1 below). The dry deposition velocity of HNO_3 is much higher during the day -when the concentrations are high- than in nighttime (Fischer et al., 2006; Phillips et al., 2006; Zhou et al., 2010). We agree, however, that the deposition is not the only reason of lower concentrations of HNO_3 in the evening. We modified the sentence "Although most of the HNO_3 comes from the daytime reaction of OH with NO_2, since the deposition rate of HNO_3 is very high, the main pathway leading to the formation of PNO_3 is the hydrolysis of N_2O_5 at night, when the temperature is sufficiently low for partitioning to the particle phase." in the Section 3.5 of the revised manuscript as:

"As seen in Figs. 6a and 6b, the daytime production of HNO_3 is higher than the nighttime production. On the other hand, the deposition rate of HNO_3 is much higher during the day than in nighttime (Fischer et al., 2006; Phillips et al., 2006; Zhou et al., 2010). HNO_3 concentrations usually show a distinct minimum during early morning hours and a maximum in the afternoon with a rapid drop near sunset (Fischer et al., 2006; Aas et al., 2012). The diurnal cycle of the modeled HNO_3 in this study shows a similar behavior with concentrations in the evening lower than the increase in nitrate concentrations at night (Fig. S12). Our results suggest that the main pathway leading to the formation of PNO_3 is the hydrolysis of N_2O_5 at night, when the temperature is

sufficiently low for partitioning to the particle phase."

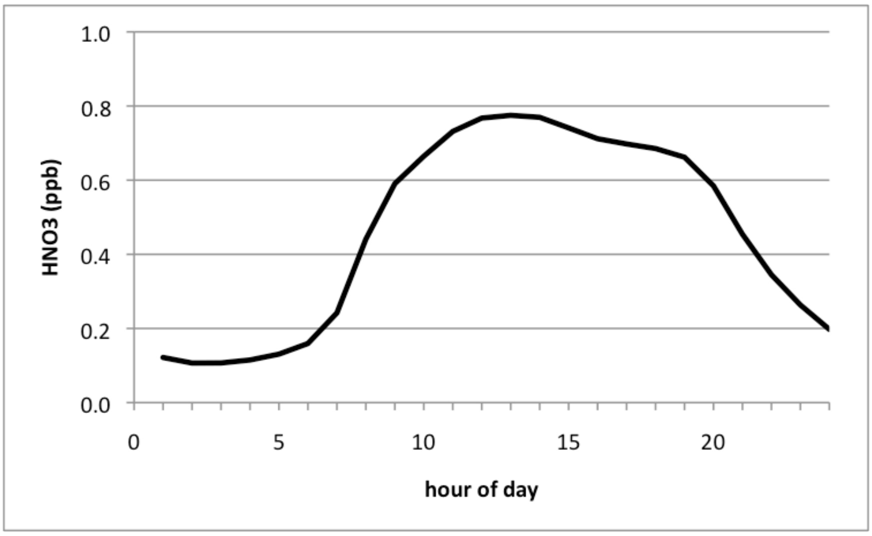

Figure 1: Diurnal cycle of modeled HNO_3 concentrations (ppb) at Payerne (June 2006) (added as Fig. S12 in the revised Supplement).

It also appears Fig. 6d (used to be Fig. 5d) changed markedly. What was the reason for this change? The revised plot decreases the apparent difference.

Fig. 5d in the previous version was only for one day (14 June) and we changed it to an average of the whole month (June) in the revised version (Fig. 6d) following the recommendation of the referees of the previous version. The difference is due to the fact that 14 June was one of the warmest days in June and therefore PNO_3 dropped sharply near zero in the early morning hours and remained very low until the sunset when it increased again. As a result of averaging all days, the figure became smoother.

They should still make sure it is clear to the reader that the PSAT result is not the same as the source impact. This is clear in Fig. 7. Given that the nitrate is ammonium nitrate, either the availability of nitrate or ammonium controls formation. In Fig. 7, it shows that most of the NH4 is from SNAP10, while little of the NO3 is from SNAP10 (largest contributor is SNAP7). If one were to remove SNAP10 emissions, much of the PNO3 would be removed. Thus, sentences like "Road transport (SNAP7) was predicted to be the most important source for PNO3 with the largest contribution during the cold season…" should be given context, potentially in the conclusions, as well as further discussion of this when PSAT is originally discussed. For example, the statement "While PSAT quanitifies the source of the the ammonium or nitrate in the PM2.5, this is not the same as the source impact as the system may be limited by another component. For example, removing SNAP10 emissions would not only reduce ammonium, but nitrate as well."

We assume that the referee means not Fig. 7, but Fig. 8 where contributions from various categories to PNO3, PSO4 and PNH4 are shown. One has to keep in mind that PSAT provides PM attribution to source regions and categories for a given emissions matrix, but does not provide quantitative information as to how PM contributions would change as emissions are altered because chemical interactions are nonlinear. We made a few modifications in the revised text to make this clearer:

In Section 2.2 : *One has to keep in mind that PSAT provides a PM attribution to source regions and categories for a given emissions matrix, but does not provide quantitative information as to how PM contributions would change as emissions are altered because chemical interactions are nonlinear.*

In Conclusions: *One has to keep in mind that these results refer to the emissions matrix used in this study and they might be different if emissions are modified because chemical interactions are nonlinear.*

References

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