Supplement to Response to the Interactive comments on "The impact of different nitrous acid sources in the air quality levels of the Iberian Peninsula" by M. Gonçalves et al.

Anonymous Referee #3
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This manuscript presents an ambitious attempt to use a regional chemical transport model to explore the impact of several parameterized sources of HONO on air quality in Spain and Portugal. It is increasingly realized that HONO is an important OH source in both urban and rural regions, and that the chemistry of HONO is not well treated in most air quality and chemical transport models. In defense of such models, it is probably also safe to say that this chemistry is not yet well enough understood. Thus, the topic of this investigation is timely and should be of interest to several scientific communities.

Unfortunately, the present study has a significant number of shortcomings. I note that referees 1 and 2 have pointed out many such issues, which I largely agree with. On the highest level I feel that critical issues that must be addressed before publishing this work include:

- recognition and consideration of the importance of daytime sources of HONO to support relatively high mixing ratios seen through most sunlit hours in essentially all recent observational campaigns;

The authors agree with the referee regarding the need for consideration of daytime HONO sources in order to determine the key factors behind observed daytime HONO levels. Hence, the manuscript is now updated with the model scenarios examining the photolytic HONO source presented by Li et al. (2010)[1] and the corresponding discussion of the results. Details on the parameterization of the kinetics can be found in the response to Referee#1.

- explicit consideration of multiple heterogeneous sources recently shown to important in some situations;

In our manuscript, we have discussed other heterogeneous sources of HONO besides the ground surface (e.g. soot, aerosol), where the latest proposed parameterizations are expressed as available surface area provided by the said mediums. After careful calculations, however, we showed that they are not quantitatively important due to the relatively small surface available for reaction compared to ground surfaces for the Iberian Peninsula. Hence, heterogeneous reaction on aerosols is not examined in this study due to the high uncertainty in its relative importance in the atmosphere in our selected modeling domain.

- model output must be assessed against observations.

[1] Li et al. (2010). Impacts of HONO sources on the photochemistry in Mexico City during the MCMA-2006/MILAGO Campaign, Atmos. Chem. Phys., 10, 6551-6567, 2010.

This last point may be the most important, as noted several times by referee 2 (how can one claim that one model scenario is "better" than another with no objective truth for comparison?). The authors suggest that it is not possible to validate the different model runs due to lack of HONO observations in the study region (and specifically during the one day episode of interest). While it would doubtless be informative to simulate Oct/Nov 2008 and compare model estimates to DOMINO observations, it is not clear that this would help to establish model skill in urban areas with stronger sources. Therefore, it may be that simulating HONO on regional scale as large as the Iberian Peninsula may be premature, pending observational data base for the same region.

To reiterate the main purpose of our study, we aim to examine relative contribution of each HONO sources and the consequent impact on other secondary pollutants, rather than to reproduce quantitatively observed HONO mixing ratios. In order to embark upon such task of reproducing ambient HONO levels, not only historical HONO measurement campaigns in the Iberian Peninsula urban regions are required, proper meteorological episodes and emissions inventory development will be necessary. As the referee mentioned, much uncertainties still exist in regards to HONO sources, and thus the scope of such project is too great at the current state of the scientific community. In an effort to close such grand gap, we examine not only various state-of-the-art parameterizations for HONO heterogeneous processes, but by also including emissions and daytime sources, we can assess the relative importance of the chemical production of HONO versus direct emissions. The comparison of our model results with the range of urban levels registered worldwide up to date (Table 3) is only done for qualitative purposes. The outcome of this study will then be useful for future works in determining which processes should be focused on, and which sources can be neglected.

Finally, Sörgel et al. (2010) measurements are taken at a rural region during wintertime, so its lack of applicability in this work, as expressed by Referee#3, has lead to the removal of this citing for our manuscript.

However, even if HONO observations were already available to test the model, leaving it out multiple likely sources is bound to overestimate the importance of the favored sources that are implemented (e.g., direct emissions).

This study now includes daytime photolytic source of HONO. As for processes on aerosols, we studied NO_2 hydrolysis on aerosol surfaces exclusively, but after careful calculations we showed that it is not quantitatively important due to the relatively small surface available for reaction compared to ground surfaces. Detailed discussion on the contribution of different sources to HONO levels have been addressed in the item by item response to Referee#1. In summary, we find that heterogeneous chemistry sources can contribute up to 35% to HONO levels in urban areas. Direct emissions for the specific case of Madrid still constitutes the primary source of HONO in our model, even in the case where a new photolytic source is introduced. Nevertheless, we believe that the current implementation of the diurnal source underestimates atmospheric levels, as discussed in the response to Referee#1.