

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 #4

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General Comments:

I agree with the arguments that were already raised by reviewers 1-3.

In my view the paper has little new to add to the discussion that is going on with respect to the importance of HONO for photochemistry. Moreover, it falls back behind the findings given in Vogel et al. (2003) and Sarwar et al. (2008). The paper of Aumont et al. (2003) should be considered and be added to the list of references.

The authors empathize with the referee's concerns, thus daytime source and updated photochemistry of HONO by Li et al. (2010)¹, along with the respective discussion of the results, are now added to the revised manuscript. Details on the methodology of these updates can be found in the response to Referee#1. Justification on the decision to choose parameterization by Li et al. (2010)¹ over other studies related to photolytic source of HONO can also be found in the responses to Referee#1.

The paper lacks from two major shortcomings. Firstly, it does not take into account photolytic sources of HONO which were suggested to be of great importance by previous studies (many of them are cited in the paper). Secondly, it does not contain any comparison of observed and measured diurnal cycles of HONO. It is hard to understand what can be learned from a comparison of the modeled HONO concentration of a single day in June 2004 with averaged measured concentrations for a period in November-December 2008.

A photolytic source of HONO is now discussed in this work. As for the issue with lack of comparisons with observations, it should be reiterated that the main purpose of our study is to examine relative contribution of each HONO sources and the consequent impact on other secondary pollutants, rather than to quantitatively reproduce observed HONO mixing ratios. The major obstacle we face in modeling ambient HONO levels lies with uncertainties regarding identified HONO sources and the lack of HONO measurement campaigns in the Iberian Peninsula. In an effort to close such gap, we compare various state-of-the-art parameterizations for HONO heterogeneous processes along side with direct emissions and daytime sources. Our model results are evaluated against the range of urban levels registered worldwide up to date (Table 3) for qualitative purposes only. The outcome of this study will then be useful in determining the direction and focus of future works. Finally, since Sörgel et al. (2010)¹ measurements are

¹ Sörgel et al., 2010. What determines the HONO daytime source? First results from field measurements in south west Spain, Geophys. Res. Abs., 12, EGU2010-13137-1, 2010.

obtained at a rural region during wintertime, its lack of applicability in this work mainly focused on urban regions, and the confusion it has caused for the referees, have lead to the removal of this citation from the revised manuscript.

If the authors have data for that period they should perform model runs for that period.

Without doing that the paper describes a sensitivity study on HONO formation taking into account direct emissions of HONO and their heterogeneous formation at the surface. However, it might be that the study is still of interest as it shows the influence of relative humidity and that not only ozone concentrations but also the PM2.5 concentrations are sensitive to the additional HONO sources.

The modeling episode was carefully selected to represent the worst case scenario for the Iberian Peninsula in order to most effectively examine the impact of HONO sources on other secondary air pollutant. As stated previously, this study does not aim to reproduce observed mixing ratios, but rather, to perform a sensitivity study of different HONO source types to input parameters in air quality models, as the referee suggested.

Minor comments:

It would be very helpful for the reader if the abbreviations of the different model runs are more intuitive (Table 2)

In principle, names for the different cases are maintained. A new case is added and named as: HCPhot, referring to the photoenhanced heterogeneous conversion of NO₂ to HONO.

A different proposal could be: BASE (no HONO at all), BASEA (base case + heterogeneous chemistry on aerosols), EM08 (0.8% HONO/NO_x ratio on emissions), EM2 (2% HONO/NO_x ratio on emissions), HC1 (heterogeneous chemistry with kinetics derived from k1), HC2 (heterogeneous chemistry derived from k3), HC3 (heterogeneous chemistry derived from k4). But authors do not believe that this alternative nomenclature would be more clarifying than the previous one.

Fig.3. The labels of the legend (colour code) are hard to read. Figure 3 (d) please change into ppt and modify the colour code to highlight the spatial pattern of HONO. What do you mean by 'concentrations estimated by'?

The changes have been introduced. The wording "as estimated by" has been changed to "predicted by ... model" to avoid confusion.

Figs. 4-10. The character size for axis and legend labels is too small.

The changes have been introduced.

Fig. 9. What are the units of the values that are shown? The colour code should be modified to depict the spatial pattern.

Units ($\mu\text{g m}^{-3}$) are now indicated in the Figure legend. Color scales have also been improved.

Fig. 10. What do you mean by 'estimated by'? Are the results of the model estimations? Are the units given in Figure 10 correct? Do you have any comparisons with observations?

The wording "as estimated by" has been changed to "predicted by ... model" to avoid confusion. There was an error on the labeling of Figure 10, which is corrected in the revised manuscript. Units of the figure are $\mu\text{mol m}^{-3}$. There are no available observations of hourly $\text{PM}_{2.5}$ components concentration for the 18 June, 2004, therefore comparison with observations is not possible for this specific case. Model evaluation parameters have been derived for PM_{10} against observations from ground air quality stations in the Iberian Peninsula (refer to item by item response to Referee#1 for details). However, those evaluation parameters do not provide specific information on the model performance for the predictions of fine fraction of PM, neither its composition.

The results shown in this figure are quite interesting. Especially the differences for Cangas are quite substantial. Nevertheless, this is hard to understand as no significant changes in nitrate were found (208205, line 4). What means no significant changes?

Changes in aerosol concentrations between the BASE and BASENA cases are below $0.6 \mu\text{g m}^{-3}$. For details and explanation on the composition changes, please refer to item by item response to Referee#2 comments.