Atmos. Chem. Phys. Discuss., 10, C14094–C14098, 2011
www.atmos-chem-phys-discuss.net/10/C14094/2011/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "The impact of different nitrous acid sources in the air quality levels of the Iberian Peninsula" *by* M. Gonçalves et al.

M. Gonçalves et al.

maria.goncalves@upc.edu

Received and published: 23 February 2011

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.

General comments:

The authors gratefully acknowledge all comments made by all referees. We consider them very useful and we have carefully addressed them in order to improve our manuscript quality. Due to the number of common remarks between the referees, we have prepared a general unified response where we address their major concerns. Item by item responses to comments from Referees #1, #2, #3 and #4, which include description of the main changes that are now part of the revised manuscript, are in-

cluded in separated comments.

Overall, the reviewers recognize the significance of this study and the associated large uncertainties on identifying and quantifying atmospheric sources of HONO. Their concerns, on the other hand, can be summed up by two major categories: 1) the lack of well-known sources of HONO, namely daytime sources, that may lead to the overestimation of the importance of favored sources such as direct emissions, and 2) the need for comparisons with observations.

HONO peaks have been observed to occur during nighttime, mostly during the hours just before sunrise, hence our initial approach was to examine the nocturnal sources such as emissions and heterogeneous chemistry in the urban atmosphere. In light of the recent measurements of persistent HONO levels during daytime, as emphasized by the reviewers, our methodology has been revised to address these issues related to the proposed daytime processes. In addition to the revision of the state-of-the-art diurnal sources, we added a photolytic process in our model and examined its relative contribution and importance to predicted HONO and other secondary pollutant levels.

The proposed daytime sources of HONO include photolysis of absorbed HNO3 (Zhou et al., 2003), photolysis of absorbed NO2 on humic acid films (Stemmler et al., 2006), photolysis of nitro-phenols (Bejan et al., 2006) and photolysis of NO2 on soot surfaces (Monge et al., 2010). Renoxification processes (Rivera-Figueroa et al., 2003) and excited NO2 chemistry (Li et al., 2008,2009) are also suggested as potential HONO sources. Based on these works, studies such as Sarwar et al. (2008) and Li et al. (2010) have developed corresponding parameterizations suitable for 3-D air quality models. Of these, we found the methodology by Li et al. (2010) to be most comprehensive, and thus the same HONO photolysis source as a function of NO2 deposition velocity, model surface to volume ratio, and NO2 uptake coefficient was tested. The results, in short, do not reflect the observed persistent daytime HONO level from ambient measurements, reiterating the existing uncertainties of ambient HONO sources. Even in the presence of the newly implementation of daytime photolytic production of HONO,

ACPD
10, C14094–C14098, 2011

direct emissions still dominate as the key contributor to the predicted HONO levels in the Iberian Peninsula. While this may be interpreted as contradictory to previous studies that indicated emissions should not be the dominant HONO sources, our results in fact simply reveal the possible inefficiency of the current parameterization method available for HONO production outside of heavily polluted urban regions, where greater range of geographical and meteorological parameters should be considered. Detailed discussions of these points are now added to the revised manuscript, as well as a comparison of the impacts of the additional HONO sources in the Iberian Peninsula against others shown in modeling studies elsewhere.

In regards to the concerns relating to the lack of validation of our model results to ambient observations, we want to emphasize on the fact that the WRF-ARWv3.1.1/HERMES-2004/CMAQv4.7 modeling system and selected episode in this study has been used extensively to assess the air quality levels in the Iberian Peninsula, both in the hindcast and forecast modes (example studies are given in the manuscript). In other words, the performance of the model has been validated in numerous previous occasions. The goal of current study is not further model performance evaluation, but to quantify the relative contribution of various HONO sources, and to assess the possible resulting effects on secondary pollutants predictions. The model evaluation for O3, NO2 and PM10 in the Iberian Peninsula as Supplementary Material is now included in the revised manuscript. This work aims to provide an assessment of HONO effects on the Iberian Peninsula air quality and to provide a reference for future studies on this matter. This work could be considered as one of the first steps in a long path to improve models' uncertainties.

The selection of 2004 is conditioned fundamentally by the emissions inventory, and the specific day, 18 June, is selected under the worst-case-scenario perspective. It is representative of numerous situations of air pollution in the Iberian Peninsula, and provides a framework to assess changes in model predictions due to the addition of new HONO sources in a situation when they can be especially relevant (the air quality

ACPD
10, C14094–C14098, 2011

thresholds set by the EU are commonly exceeded in those typical summertime events). Unfortunately, HONO observations are not available for our episode; therefore the qualitative comparison with DOMINO data has been removed from the last version of the manuscript to avoid confusion.

With the new additions to the revised manuscript addressing the various issues and following the suggestions of the reviewers, this work has improved significantly in quality and value. As mentioned in the beginning, detailed item by item response to the reviewers' comments and corresponding edits made to the article can be found in the Supplementary file, where the original comments are in black and our responses in blue.

Again we thank the reviewers for their generous and valuable contributions to this work.

References:

Bejan, I., et al., 2006. The photolysis of ortho-nitrophenols: a new gas phase source of HONO. Phys. Chem. Chem. Phy., 8, 2028-2035.

Li, et al., 2008. Atmospheric hydroxyl radical production from electronically excited NO2 and H2O, Science 319, 1657-1660.

Li, et al, 2009. Response to comment on atmospheric hydroxyl radical production from electronically excited NO2 and H2O, Science 324, 336.

Li et al., 2010. Impacts of HONO sources on the photochemistry of Mexico City during the MCMA-2006/MILAGO campaign. Atmospheric Chemistry and Physics 10, 6551-6567. doi:10.5194/acp-10-6551-2010

Monge et al., 2010. Light changes the atmospheric reactivity of soot. PNAS. www.pnas.org/cgi/doi/10.1073/pnas.0908341107.

Rivera-Figueroa et al., 2003. Laboratory studies of potential mechanisms of renoxiïňĄcation of tropospheric nitric acid. Environmental Science & Technology, 37, 548-554.

ACPD

10, C14094–C14098, 2011

Sarwar et al., 2008. A comparison of CMAQ HONO predictions with observations from the Northeast Oxidant and Particle Study. Atmospheric Environment 42, 5760-5770.

Stemmler et al., 2006. Photosensitized reduction of nitrogen dioxide on humic acid as a source of nitrous acid. Nature 440 (9), 195 doi:10.1038/nature04603

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 28183, 2010.