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 #2

Received and published: 22 December 2010

General comments:

The study uses a 3-D air quality model to simulate atmospheric HONO concentrations and their impacts on air quality over Iberian Peninsula. It uses three sources of HONO in the model: gas-phase chemistry, emissions, and a heterogeneous reaction. Two different HONO emissions rates and two different parameterizations of the heterogeneous reaction are used. HONO chemistry is not well known and the current 3-D air quality models do not accurately predict HONO concentrations. The manuscript attempts to quantify HONO production from different sources and their impacts on model results. It also incorporates the impact of relative humidity on HONO production. Publication is recommended. However, it lacks some important issues: simulation is too short (1-day simulation), no comparison with observed HONO data, no comparison of model predictions of other pollutants with observed data and some known chemical reactions are omitted in the study. Thus, the manuscript needs a major revision

The day selected for the simulation is representative of summertime air pollution episodes of anthropogenic origin in the study area. It is selected under the worst case scenario perspective and corresponds to a synoptic meteorological pattern frequent in the Iberian Peninsula and normally associated to highly polluted events. Our results provide a reference for the impacts of HONO addition in air quality modeling in the Iberian Peninsula in those cases. They are usually characterized by high O_3 and PM concentrations, registering levels above the European Union air quality thresholds for human health protection. Thus, it is extremely important to improve model's predictions in those cases. The characterization of HONO effects on different meteorological situations and for longer periods it is not within the scope of this work, nor is the reproduction of observed HONO levels within the Iberian Peninsula, as no urban measurements of HONO mixing ratios are currently available.

HONO measurements shown in the manuscript correspond to a rural location during winter time; hence they are only useful as a reference for our purposes. Our main concerns are, first, to improve nighttime HONO build-up representation in the model in order to better characterize OH sources during the early morning; second, to focus specifically on urban regions, where HONO addition could provide a better representation of secondary pollutants formation. HONO clearly affects O_3 and PM production in urban plumes, but we also noticed that sulfates and ammonia concentrations are affected by the increased OH radical concentration in rural environments, therefore this effect is discussed in the manuscript.

In addition, a description on the model performance in terms of O_3, NO_2 and PM_{10} prediction is included as supplementary material (see item by item response to Referee#1); specific evaluation of HONO is not feasible in our case due to the lack of suitable observed data.

Finally, Referee#2 argues that the model lacks of some important chemical processes leading to HONO production. As mentioned in the response to Referee#1, a photolytic HONO source has been added to our model and results are included now in the manuscript. Processes on aerosols, however, remain highly uncertain in their relative importance in the atmosphere. We have considered NO_2 hydrolysis on aerosol surfaces exclusively, and showed that it is not quantitatively important due to the relatively small surface available for reaction, compared to ground surfaces.

Specific comments

Section 1 – Introduction

Page 28187 Statement

Recent findings suggest that the importance of Reaction (R7) would be its role on the detected HONO levels in diesel vehicles exhaust (Gutzwiller et al., 2002).

Comment: The sentence is not clear.

NO_2 reduction on aerosol surfaces is one of the potential heterogeneous sources of HONO (R7), nevertheless its importance in the atmosphere has been questioned due to the fast deactivation of aerosol surfaces. A recent study from Gutzwiller et al. (2002)[4] points out that diesel exhaust contains high concentrations of semi-volatile organic compounds that can potentially enhance the heterogeneous NO_2 reduction to nitrite, which below specific pH conditions could release HONO into the gas phase. They suggest that this process could be an important HONO source in the atmosphere, providing an estimate of 0.023 heterogeneously produced HONO by primary NO_x emitted. The comment on the manuscript is now clarified as:

"*Soot surfaces have been proposed as effective substrates for R7 (Ammann et al., 1998). The fast deactivation of the aerosol surface, and the smaller available surface area compared to buildings or vegetation surfaces, raise the question of the relative importance of R7 on aerosols to the atmospheric HONO budget (Sarwar et al., 2008). Recently, Gutzwiller et al. (2002) suggested that R7 could be enhanced in diesel exhaust due to the presence of semi-volatile organic compounds, reporting that a fraction of 0.023 of the NOx emitted can be heterogeneously converted to HONO.*"

Section 2.1 – Modeling framework

Page 28189 Statement After a thorough analysis of O_3, NO_2 and $PM_{2.5}$ observations in Spain for the year 2004 (provided by the Spanish Air Quality Surveillance, CSIC and EMEP networks), 18 June 2004 is selected as the test episode for this study.

Comment: Only one day simulation is conducted. While the model can provide good performance for a single day; it may or may not provide similar results on other days. One day simulation is to narrow to understand the impact of HONO on model predictions; longer simulation period is needed. For example, Li

et al. (2010) recently used WRF-CHEM model to simulate HONO in Mexico City. They completed model run for 6 days and compared predictions with observed data.

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

As mentioned in the response to the general comments from Referee#2, the selected day is representative of poor air quality conditions in the Iberian Peninsula. Our study focuses on the relative contribution of various proposed HONO sources and the subsequent resulting impact on secondary pollutant levels, rather than the validating model performance in predicting observed HONO mixing ratios. Thus, the length of the simulation period is not crucial.

18 June 2004 is characterized by high air pollution levels of anthropogenic origin. Meteorological conditions correspond to a western recirculation in the synoptic scale. These conditions dominate 45% of the annual and 78% of the summertime transport patterns over the coastal Mediterranean areas and 36% of the annual and 45% of the summertime situations in the central-continental areas of the Iberian Peninsula, as studied by Jorba et al., 2004[1]. Synoptic recirculations are usually associated to local to regional pollution episodes, characterized by the accumulation of pollutants and poor air quality conditions (Jiménez et al., 2006[2]; Gonçalves et al., 2009[3]). Therefore, even if the simulation is performed for a specific day, it is considered as representative of typical summertime pollution episodes in the Iberian Peninsula.

Section 2.2 – Nitrous acid emissions

Page 28190 Statement However, the latest guidelines for the estimation of emissions of the European Environmental Agency (EEA/EMEP-CORINAIR, 2009) and the speciation profiles provided by the US Environmental Protection Agency (US-EPA, 2008) do not consider on-road traffic as a potential HONO source.

Comment: Speciation profiles provided by the US Environmental Protection Agency (US-EPA, 2008) did not specifically focus on HONO speciation from NOx. CMAQv47 (which the authors used here) considers HONO from on-road motor vehicles and uses 0.8% of NOx as HONO.

More information can be found at: www.epa.gov/ttn/chief/emch/index.html#2005. Specific file: ftp.epa.gov/EmisInventory/2005v4/ancillary_smoke/ancillary_2005v4_smokeformat.zip

HERMES-2004 emissions model follows both the EEA/EMEP-CORINAIR emissions inventory guidebook and the US-EPA (2003) speciation profiles, therefore, our BASE case does not account for HONO

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[1] Jorba et al., 2004. Cluster Analysis of 4-Day Back Trajectories Arriving in the Barcelona Area (Spain) from 1997 to 2002, J. Appl. Meteorol., 43(6), 887–901, 2004.

[2] Jiménez et al., 2006. Multiscale modelling of air pollutants dynamics in the northwestern Mediterranean basin during a typical summertime episode, J. Geophys. Res., 111, D18306, doi:10.1029/2005JD006516, 2006.

[3] Gonçalves et al., 2009. Contribution of atmospheric processes affecting the dynamics of air pollution in South-Western Europe during a typical summertime photochemical episode. Atmos. Chem. Phys., 9, 849–864, 2009

emissions. Nevertheless, recommendations from the Models-3 community are considered when defining the different emission scenarios, as indicated in the manuscript. The EM08 scenarios follow the Models-3 guidelines, which are based on Kurtenbach et al. (2001)[7].

Statement HERMES-2004 for this study follows the EEA/EMEP-CORINAIR methodologies for estimating emissions (EEA/EMEP-CORINAIR, 2009) and applies the US-EPA (2003) speciation profiles for NO_x. Currently, the recommendation from the US-EPA allocates 95% of total NO_x as NO and 5% as NO_2 for on-road traffic emissions, and 90% as NO and 10% as NO_2 for all other sources.

Comment: This is old. Currently, USEPA uses 90% of NO_x as NO and 10% of NOx as NO_2 for all sources except motor vehicles which uses 90% as NO, 9.2% as NO2, and 0.8% as HONO.

More information can be found at: www.epa.gov/ttn/chief/emch/index.html#2005. Specific file: ftp.epa.gov/EmisInventory/2005v4/ancillary_smoke/ancillary_2005v4_smokeformat.zip

HERMES uses US-EPA (2003) speciation profiles for NO_x, therefore no HONO emissions are included in the BASE cases. The manuscript, however, clarifies that the latest recommendations of Models-3 and CHIMERE community vary from those used in our model and already suggest using 0.08 HONO/NOx ratio in emissions, an additional comment to clarify that US-EPA recommendations are analogous to those from Models-3 is now included in the manuscript, as follows:

"[…]The latter (Kurtenbach et al., 2001) results have already been adopted by several modeling communities, such as the Models-3 Community from US-EPA and the CHIMERE community in France (Sarwar et al., 2008; INERIS, 2009). The Spanish vehicle fleet in 2004, on the other hand, is composed of 52% of gasoline vehicles and 48% of diesel fuelled vehicles (DGT, 2010), so a higher HONO/NO_x ratio from on-road traffic is expected.

HERMES-2004, used for this study, follows the EEA/EMEP-CORINAIR methodologies for estimating emissions (EEA/EMEP-CORINAIR, 2009) and applies the US-EPA (2003) speciation profiles for NO_x. It allocates 95% of total NO_x as NO and 5% as NO_2 for on-road traffic emissions, and 90% as NO and 10% as NO_2 for all other sources."

Statement: In order to include HONO emissions two different emissions parameterizations are examined in this work: (1) 0.8% of NOx from mobile sources, the most widely accepted HONO/NOx emission ratio; (2) 2% of total NOx for all the anthropogenic sources, an upper limit based on the early studies by Harley (1996) that is currently used by the California Air Resources Board

Comment: Please describe the details of NOx speciation. If 0.8% of NOx from mobile sources are taken as HONO, how the remaining (99.2%) NOx emissions are speciated into NO and NO2. Is NO or NO2 adjusted for mass conservation? Similarly, if 2% total NOx for all the anthropogenic sources are taken as HONO, how the remaining (98%) NOx emissions are speciated into NO and NO2. Is NO or NO2 adjusted for mass conservation?

Additionally, 2% of total NOx for all anthropogenic sources as HONO may be too high that may produce artificially elevated HONO predictions. The authors cited a reference (Harley, 1996) which is 15 years old

and not published in peer-reviewed literature. The role of heterogeneous reactions may not have been fully realized at that time. The authors should substantiate the use HONO = 2% of all NOx by citing peer-reviewed published literature. Specifically, the authors should cite any work that focuses on the measurement of HONO from power plants, boilers, turbines, etc.

HONO emissions are added as 2% or 0.8% of NO_x. Speciation of NO_x in the new scenarios is made as follows:

> EM08: 0.8% HONO; 89.3% NO; 9.9% NO_2.

> EM2: 2.0% HONO; 79.4% NO, 9.8% NO_2 for mobile sources and 2.0% HONO; 93.1% NO, 4.9% NO_2 for other sources.

The scenarios with HONO as 2% of total NO_x emissions are taken as an upper limit. This specific HONO to NO_x emissions ratio is not based on experimental data, but it is defined in order to assess the HONO effects considering that the model lacks of currently unknown sources. In addition this high HONO/NO_x ratio is comparable to the 0.023 HONO/NO_x derived from the Gutzwiller et al. (2002)[4] work for diesel exhaust, and already included in modeling works in urban areas, namely the WRF-Chem modeling study for Mexico City from Li et al. (2010)[3]. These aspects are clarified in the manuscript:

"In order to include HONO emissions two different emissions parameterizations are examined in this work: (1) 0.8% of NO_x from mobile sources, the most widely accepted HONO/NO_x emission ratio; (2) 2% of total NO_x for all the anthropogenic sources, an upper limit introduced to assess possible effects of unknown HONO sources, based on the early studies by Harley (1996) that is currently used by the California Air Resources Board. This ratio is comparable to the 0.023 HONO to NO_x ratio introduced by Li et al. (2010) in order to assess the effects of HONO production via reduction of NO_2 on semi-volatile organic compounds emitted with diesel exhaust (Gutzwiller et al., 2002)."

Section 2.4 – Heterogeneous chemistry on surfaces

Page 28193 Comment: What value of A (the correction factor in eqn. 4) was used to derive k_2 presented in eqn 5. Should RH be fractional relative humidity rather than percent relative humidity?

Please provide the deposition velocity for the chamber. Please double check equation (5) so that it yields 0.22 ppb of HONO/min/NO_2(ppm) when appropriate values are used. Many other HONO chemical reactions have been suggested in the literature. Gutzwiller et al. (2002) suggested that HONO can be formed from the interaction of NOx from diesel engines and semi-volatile organic compounds. Li et al. (2010) used this procedure and suggested it can produce a major fraction of predicted HONO in Mexico City. Rivera-Figueroa et al. (2003) suggested that adsorbed HNO_3 can react with NO to produce HONO. Zhou et al (2003) suggested HONO production from adsorption of HNO_3 on ground. Bejan et al (2006) suggested HONO production from the photolysis of nitrophenol. Stemmler et al. (2006, 2007) suggested that NO_2 can potentially react with humic acid to produce HONO. Li et al. (2008, 2009) suggested that excited NO_2 chemistry can generate HONO. None of these pathways is discussed and their possible impacts on HONO in Iberia Peninsula are ignored.

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

Zhou, X., et al., Nitric acid photolysis on surfaces in low-NOx environments: significant atmospheric implications. GRL 30(23), 2217, doi:10.1029/2003GL018620.

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

Stemmler, et al, 2006. Photosensitized reduction of nitrogen dioxide on humic acid as a source of nitrous acid. Nature, 440, 195-198.

Stemmler, et al, 2007. Light induced conversion of nitrogen dioxide into nitrous acid on submicron humic acid aerosol. Atmospheric Chemistry & Physics, 7, 4237-4248.

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 in Mexico City during the MCMA-2006/MILAGO Campaign, Atmospheric Chemistry and Physics, 10, 6551-6567.

"A" is the dependence factor we are looking for in Eq. 4, which is derived as 9.7×10^{-5}. The deposition velocity in order to estimate A is 0.04 cm s^{-1} and the RH is expressed in %. We must clarify here that we've taken the stoichiometric factor, 0.5, into consideration, therefore:

$$\frac{d[HONO]}{dt} = 3.66 \times 10^{-6} \frac{ppm\ HONO}{ppm\ NO_2\ s} [NO_2]\ ppm\ NO_2 = A \cdot 0.5 \cdot v_{NO_2} \cdot RH \cdot \left(\frac{S}{V}\right) [NO_2] \frac{ppmHONO}{s}, \text{ and } A = 9.75 \times 10^{-5}$$

This aspect is currently clarified in the manuscript.

The authors agree with Referee#2 comment on the additional HONO sources. As already noted in Referee#1 response, we had originally focused on nighttime processes yielding HONO in significant amount (heterogeneous chemistry and emissions). Due to the Referee's comments and suggestions, we've added an additional case in our runs considering also photolytic sources in the revised manuscript. The discussion on the selection of those additional sources is now included in the manuscript, a highlight of main changes has been reproduced in response to Referee#1 (a) General Comment.

Section 3.1 – Air quality levels in the Iberian Peninsula during 18 June 2004 Page

28195 Statement: The poorest air quality conditions occur in the urban plumes from the largest cities in the Iberian Peninsula. In particular, downwind areas from Madrid and Barcelona show concentrations of O3 above 100 ppb from 14:00 to 16:00UTC (Fig.3a)

Comment: Local times are easier for readers than UTC. Spain is in GMT+2 in summertime. Conversion has been made now in the revised manuscript.

Section 3.2 – Impact of the additional sources on HONO levels

Page 28197 Statement: The introduction of HONO emissions in the model raises the overall HONO levels and improves the predicted hourly profiles.

Comment: No comparisons have been made with any observed data; thus it is not clear how predicted hourly profiles improve.

Profiles predicted by the gas-phase chemistry alone show a peak in HONO levels around midday. These BASE cases fail to reproduce the HONO build-up during nighttime and the decrease in HONO levels with sunrise. When additional sources are added, modeled HONO profiles show a peak in the early morning and higher concentrations during nighttime, as expected if we review observed HONO values in different areas worldwide (for a more detailed description, please refer to item by item response to Referee #1). Thus, the improvement is found through the diurnal trend of the daily HONO profile, and not quantitative comparisons with observations, which are not available and not crucial to this study as previously discussed.

Statement Specific measurements for the Iberian Peninsula region are needed in order to quantify the deviation of model predictions from reality.

Comment: Measured HONO data in Iberian Peninsula are presented in Figure 6 for October/November 2008. Model simulations for this time period can be performed and predicted HONO can be compared to observed data in October/November 2008. Once the model evaluation for HONO is complete after comparison with observed data in 2008, then it can be applied to the June 18, 2004 episode and the impact of HONO sources on air quality levels can be evaluated. This will support the earlier statement that the introduction of HONO emissions in the model raises the overall HONO levels and improves the predicted hourly profiles.

As aforementioned, the main purpose of this work is to assess the effects of well known HONO sources in the pollutants levels in the Iberian Peninsula. A summertime extreme pollution event is selected following the worst case scenario perspective. This work focuses on analyzing the model sensitivity to new HONO sources and the changes on secondary pollutants concentration derived. Summertime pollution episodes are frequent in the Iberian Peninsula. They are normally characterized by exceedances of the EU air quality targets, especially concerning O_3 levels in downwind areas from main NO_x sources, and NO_x and $PM_{2.5}$ in urban areas. The evaluation of the uncertainties related to model predictions in such situations could be important to decision and policy makers.

HONO observations from El Arenosillo station had been taken as reference values to assess if the model was reproducing the HONO diurnal profiles. However they are not intended to perform a full model evaluation: observations are limited to a single station in a rural environment and measurements correspond to a different period from this assessed in this work. Therefore the qualitative comparison with DOMINO data has been removed from the revised manuscript.

Page 28198 Statement The HC47 parameterization for the NO_2 hydrolysis kinetics depends exclusively on the surface area to volume ratio (Eq. 1), resulting in an increase of HONO levels ranging from 200 to 800 ppt in the northern Iberian Peninsula and urban areas. The expression of HCUCI (Eq. 5), on the other hand, varies with the relative humidity in addition to S/V ratio. Compared to the HC47 case, the impact of heterogeneous HONO production in HCUCI has a smaller geographical coverage, and the HONO increases from the BASE case range between 50 and 800 ppt. Higher relative humidity (RH) occurring during nighttime (from 20:00UTC, on) results in the differences in the predicted HONO levels up to 350 ppt between the HC47 and the HCUCI parameterization (Fig. 5). Therefore relative humidity is a key factor to be considered in the parameterization of the kinetics of the NO_2 hydrolysis.

Comment: As the authors pointed out, Stutz et al. (2004) studied the dependence of HONO on relative humidity. The results presented here can be compared to those with Stutz et al. (2004). A figure of HONO versus relative humidity (similar to Figure 6 of Stutz et al., 2004) will be informative.

HONO to NO_2 ratio is plotted against relative humidity for several locations in the Iberian Peninsula (Fig. 1).
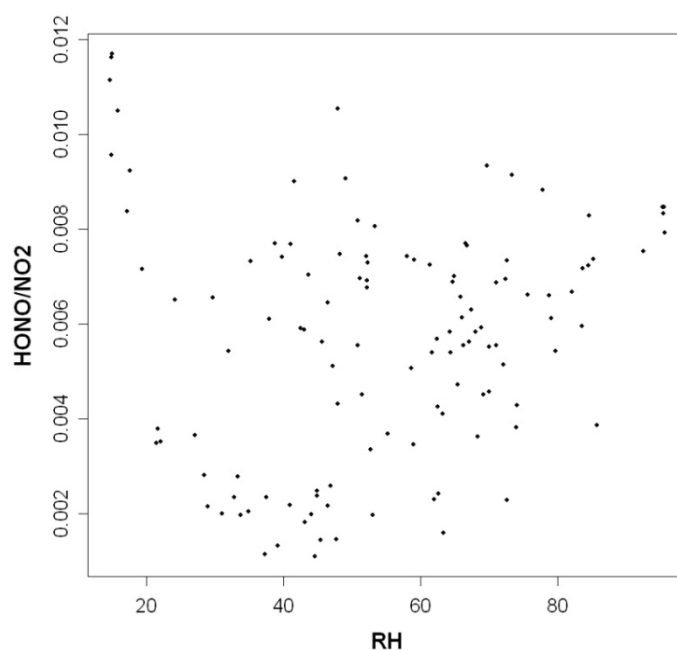

Fig. 1. HONO to NO_2 ratio as predicted in the EM08HCUCI case against RH(%) for several locations in the Iberian Peninsula.

In particular, Abanto, Eixample and Casa de Campo locations (refer to the manuscript for further details) are selected. Additionally, data from St Cugat, a relatively small city, and Compostilla, an industrial area, are included. Results show slightly increased HONO/NO_2 ratios with increased relative humidity. The trend is clearer for RH values above 40%. Ratios of 0.008 HONO/NO_2 are attributed mainly to direct emissions independently of the relative humidity. For low relative humidity values, higher ratios are observed in some cases, which would be due to high NO_2 deposition velocities. Predicted HONO/NO_2 ratios are one order of magnitude lower than those reported in Stutz et al. (2004) – Figure 6.

Page 28199 Statement Direct emissions constitute the main HONO source in all scenarios, with contributions to the HONO peak concentration ranging between 65.5% and 94.3% (EM08HC47 and EM2HCUCI, respectively).

Comment: This goes against all published literature which suggests that emissions are not the significant contributor to HONO. The authors should discuss how their findings compare with other published studies. Then they should convince readers why emissions are the most significant contributor to predicted HONO in Iberian Peninsula? What is specifically different in Iberian Peninsula than other places that results in such conclusion? In addition, a comparison of NOx and HONO emissions in Iberian Peninsula should also be presented.

Results of this study do not simply imply that emissions are the most significant contributor to ambient HONO levels. Rather, predicted HONO levels using the latest parameterization proposed in previously studies for the Iberian Peninsula domain presented in this study do not yield sufficient HONO compared to direct emissions, contrary to other works done for highly polluted areas or high effective surface parameterizations. Therefore, this work further emphasizes the needs to introduce more appropriate parameterizations of surface reactions within air quality models. Simpler parameterizations, such as those tested by Vogel et al. (2003) for photolytic sources, or Sarwar et al. (2008), could provide an effective HONO source in models in the mean time, but they risk to introduce HONO artificially in the model. More details on the characteristics of the Iberian Peninsula that lead to the high contribution to HONO levels from direct emissions are discussed below.

Results presented on Table 4 in the manuscript quantify the contribution of HONO sources for an area defined over Madrid at 600 UTC, 800 h local time. Fig. 2 shows the daily evolution of HONO levels as predicted by the model for the different cases studied over Madrid area. (Cases are defined on Table 2 in the manuscript and the new photolytic source is referred to as: EM08HCPhot)
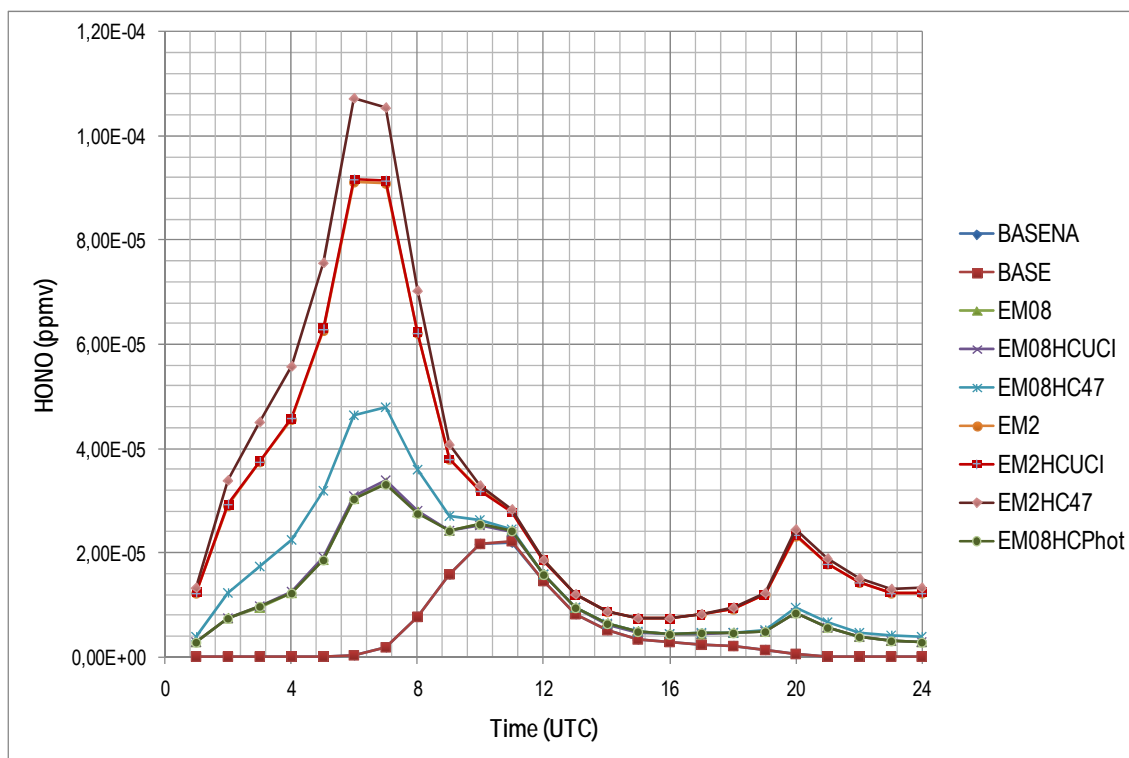
Fig. 2. HONO concentration (ppmv) averaged for an area defined over Madrid (30x30 cells). Evolution for 18 June,2004 as predicted by WRF-ARW/HERMES/CMAQ model for the BASENA, BASE, EM08, EM08HCUCI, EM08HC47, EM2, EM2HCUCI, EM2HC47 cases defined in Table 2 in the manuscript and the new EM08HCPhot case added including NO_2 photolysis on ground surfaces with kinetics parameterized as previously defined (Eq. 3, in this document)

Madrid is the largest urban area in Spain, densely populated and characterized by pollution levels highly dependent on traffic emissions. On road transport is responsible for 93% of the primary emissions of NO_x, NMVOCs, CO, SO_2 and PM_{10} (Gonçalves et al., 2009[4]) in Madrid urban area. Maximum contribution of emissions to HONO levels, 94.3%, is assessed for the EM2HCUCI case, which corresponds to the high HONO to NO_x ratio applied to compensate for the lack of additional sources in the model. In case of applying the most effective heterogeneous production parameterization (HC47) and the low HONO to NO_x emissions ratio (0.8%), the contribution of emissions is still 65.5%. When the high HONO to NO_x ratio is applied with this heterogeneous chemistry parameterization, emissions contribution is estimated to be 84.3%. The latter value is comparable to the weights obtained for different sources by Li et al. (2010) for Mexico City. In their case 75% of HONO production is attributed to reaction of NO_2 with semi-volatile organic compounds, which they parameterize applying ratio of 0.023 HONO/(primary NO_x) – based on Gutzwiller et al. (2002)[4]-. They also estimate a negligible contribution for reactions on aerosol surfaces, as it is our case for all scenarios.

The new calculations performed for the HCUCI case provide even lower contributions of the heterogeneous NO_2 hydrolysis on surfaces. Also the implemented photolytic source does not have a

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[4] Gonçalves, M., Jiménez-Guerrero, P., Baldasano, J.M., 2009. Emissions variation in urban areas resulting from the introduction of natural gas vehicles: application to Barcelona and Madrid Greater Areas (Spain). Science of the Total Environment 407, 3269-3281. doi:10.1016/j.scitotenv.2009.01.039.

noticeable impact on HONO levels. Those sources represent less than 1.0% of HONO peak concentration over the Madrid urban area in their current parameterization.

If instead of considering contributions to maximum HONO levels (at 600 UTC), we derive the contribution of different sources to nighttime and late afternoon concentrations (periods from 0:00 to 5:00 UTC and from 18:00 to 23:00 UTC, which would correspond to 2.00 – 7:00 and 20:00 – 1:00 on local time), the weight of different sources vary slightly. The specific contribution of the photolytic reaction included in the model is around 0.2% for this period. Also the HCUCI parameterization shows low contributions to HONO budget.

Table 1. Relative contribution (%) of different HONO sources to HONO levels for an area defined over Madrid region as estimated by WRF-ARW/HERMES/CMAQ for nighttime and late afternoon periods on the 18 June, 2004.

Percentage contribution of:	EM08HCUCI	EM08HC47	EM08HCPhot	EM2HCUCI	EM2HC47
Gas phase chemistry	5,0	3,3	5,0	1,5	1,3
Chemistry on aerosol surfaces	0,1	0,1	0,1	0,0	0,0
Emissions	93,7	61,8	94,7	98,1	85,2
Heterogeneous chemistry	1,3	34,8	0,2	0,4	13,5
HONO ave. concentration (ppt) from 1800 to 500 UTC	15,0	23,2	15,2	52,2	60,1

Page 28200

Statement A quantitative model evaluation cannot be performed based on the DOMINO data, because model and observations do not correspond to the same period (18 June 2004 for the WRF-ARW/HERMES/CMAQ model simulations).

Comment: Model simulations for October/November 2008 can be performed and predicted HONO can be compared to observed data in October/November 2008. Once the model evaluation for HONO is complete after comparison with observed data in 2008, then it can be applied to the June 18, 2004 episode and the impact of HONO sources on air quality levels can be evaluated

As aforementioned, the selection of the year of study is conditioned by the availability of necessary data to compute the emissions. The episode selection is performed under the worst case scenario perspective. The main goal of this paper is to assess the effects of the additional HONO sources on HONO dynamics and secondary pollutants levels below such a perspective. DOMINO data from El Arenosillo have been removed from the revised manuscript.

In addition, evaluation of HONO predictions against data for a single location and in a rural location could not provide information about the model behavior on urban areas, which are the main focus of this study due to the high pollution levels.

Statement The improvement of the HONO profiles prediction is clear when introducing HONO emissions, especially in the EM2 case, producing an increase in the early morning and nighttime levels (up to 94 ppt at 23:00 UTC).

Comment: No comparisons have been made with observed data; thus it is not clear how predicted hourly profiles improve.

Qualitative comparison against DOMINO data has been removed from the manuscript.

Page 28201 A slight overprediction is observed in the 14:00 to 16:00UTC period, which could be attributed to the specific meteorological conditions of the selected day.

Comment: No comparisons have been made with observed data; thus it is not clear how the model overpredict in the 14:00 to 16:00UTC period.

Please, refer to the previous comment and response.

Section 3.3 Impact of HONO sources on gas-phase pollutants

Page 28201 Statement In the morning, HONO emissions photolyze to produce OH and NO that lead to rapid NO_2 formation. NO_2 levels increase up to 4.0 ppb (8%) in the EM08 case and up to 9.0 ppb (18%) in the EM2 case during the morning rush hour (from 06:00 to 10:00 UTC) in the urban areas.

Comment: A figure of NO_2 profile will be helpful to readers. As pointed out earlier, HONO is produced at the expense of NO_2. Thus, when HONO emissions are estimated, NO_2 emissions should be reduced; otherwise total nitrogen species will not be conserved. Similarly, when HONO production from heterogeneous reactions is considered, NO_2 should be reduced to account for the production of HONO and consumption of NO_2.

Example of NO_2 profiles for urban locations, such as Eixample and Casa de Campo, and rural sites, such as Abanto, are depicted below (see Fig. 3). Increases in NO_2 are not attributed to the addition of emissions, but to the NO_x chemistry in the urban areas. Increase in OH release in the early morning would lead to higher oxidative potential of the atmosphere, resulting in more favorable pathway converting NO to NO_2.
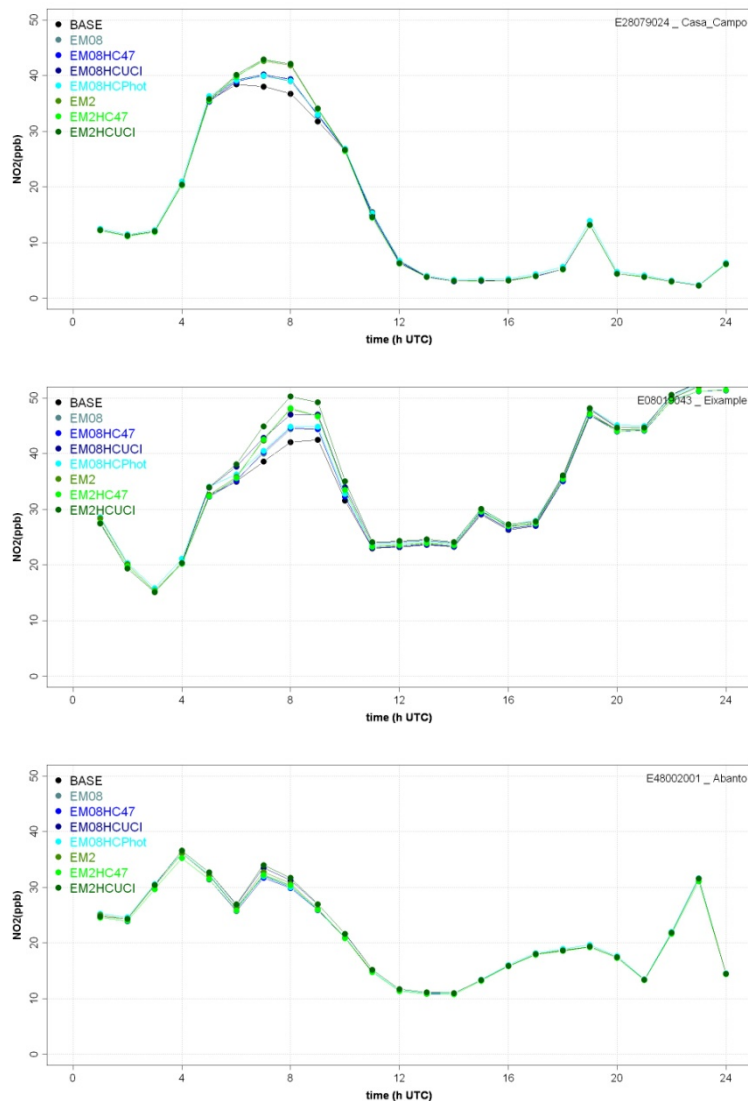
Fig. 3. NO$_2$ (ppbv) profiles in selected locations of the Iberian Peninsula as predicted by WRF-ARW/HERMES/CMAQ model for the 18 June, 2004.

Page 28202 Statement Also, the impact of the HONO emissions is shown to be larger than the impact of the parameterized ground surface heterogeneous chemistry in urban settings, where the pollutants formation is clearly dominated by on-road traffic emissions.

Comment: This goes against all published literature. Please see my earlier comments.

Please refer to previous response.

Section 3.4 Impacts of additional HONO sources on the secondary PM$_{2.5}$

Page 28203 Statement The increase in PM$_{2.5}$ levels in urban areas is mostly attributed to changes in nitrates (NO$_3$) and secondary organic aerosols (SOA). The production of OH from HONO photolysis in

urban areas in the early morning increases the oxidation capacity of the atmosphere, thus the high NOx levels from traffic emissions are likely to further oxidize and yield nitric acid (HNO_3). Gas phase HNO_3 can then partition into aerosol phase, or be absorbed onto existing aerosols to form nitrate aerosols. As expected, the HONO effect is the greatest between 06:00 and 11:00UTC, especially in those areas with high relative humidity (e.g. the Barcelona urban area), where differences in nitrate levels up to 0.7 µg m^{-3} (14%) and 0.65 µg m^{-3} (13%) in the EM08HC47 and EM08HCUCI cases are found (Fig. 9b).

Comment: Increases in $PM_{2.5}$ levels have been attributed to the increases in nitrate and SOA. Nitrate goes up by a maximum of 0.7 µg m^{-3} and SOA goes up by up 0.35 µg m^{-3}. However, $PM_{2.5}$ increases by up to 3.0 g m^3. Need to explain the cause of the additional increases in $PM_{2.5}$.

In fact, there's a mistake in the manuscript, the 2.7 µg m^{-3} increase in $PM_{2.5}$ reported for the urban areas corresponds to the EM2 case and not to the EM08 case as reported. When only 0.8% of NO_x from traffic are emitted as HONO, $PM_{2.5}$ increases up to 0.9 µg m^{-3} in urban areas, as it is now included in the manuscript

"The introduction of on-road traffic emissions of HONO (EM08) increases up to 0.9 µg m^{-3} (3.7%) $PM_{2.5}$ levels in the main urban areas."

The discussed variation of $PM_{2.5}$ compounds refers to the EM08HC47 case, which includes both heterogeneous chemistry and direct emissions. In the EM08HC47 case, maximum $PM_{2.5}$ changes are 1.4 µg m^{-3}. Results in Fig. 4 show $PM_{2.5}$ variation for the EM08HC47 case in Barcelona area at 800 UTC (10.00 h local time) and 900 UTC (11.00 h local time). The corresponding contribution of nitrate, sulfate, secondary organic aerosols and ammonia in the $PM_{2.5}$ fraction is also shown. Nitrates and secondary organic aerosols are mainly responsible for the change in aerosols levels, although ammonia and sulfate concentrations also vary and fill the gap to reported $PM_{2.5}$ changes (up to 1.4 µg m^{-3}).

On the other hand, increases of 3.0 µg m^{-3} are observed for the EM2 case in power plant plumes in the northern IP (as discussed in the manuscript). There, the fractions of $PM_{2.5}$ showing largest changes are sulfate and ammonia (see Fig. 9 in the manuscript).

$PM_{2.5}$
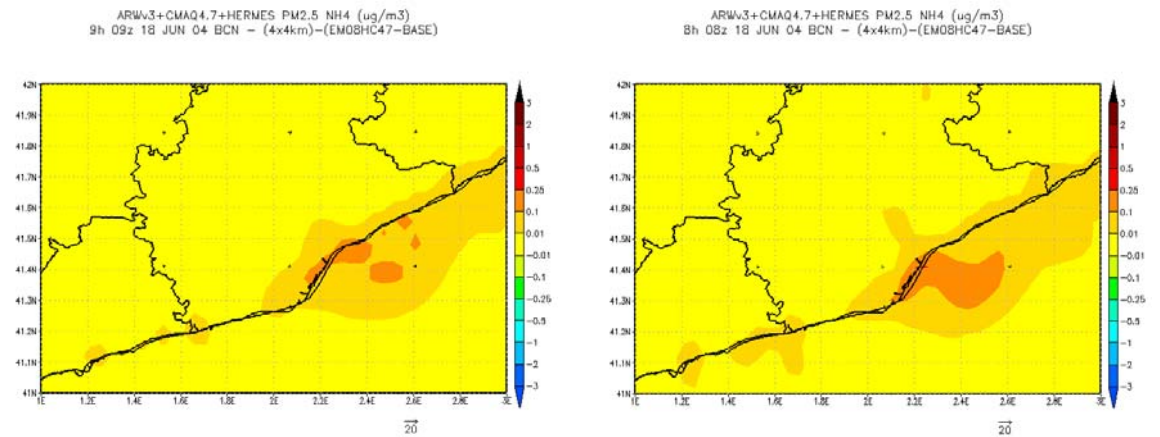
0800 UTC/1000 (local time)

0900 UTC/1100 (local time)

14
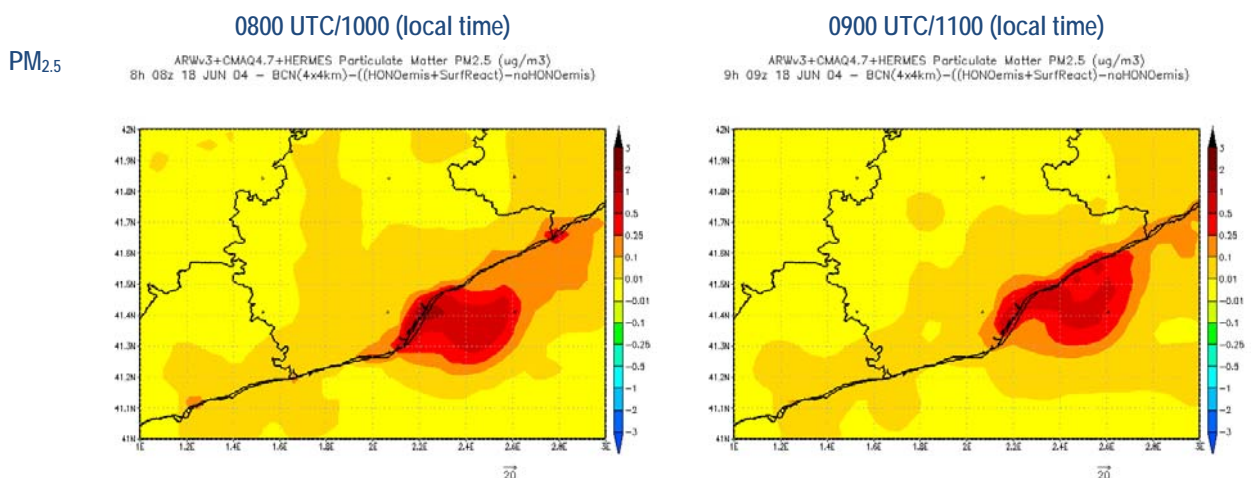
NO₃⁻
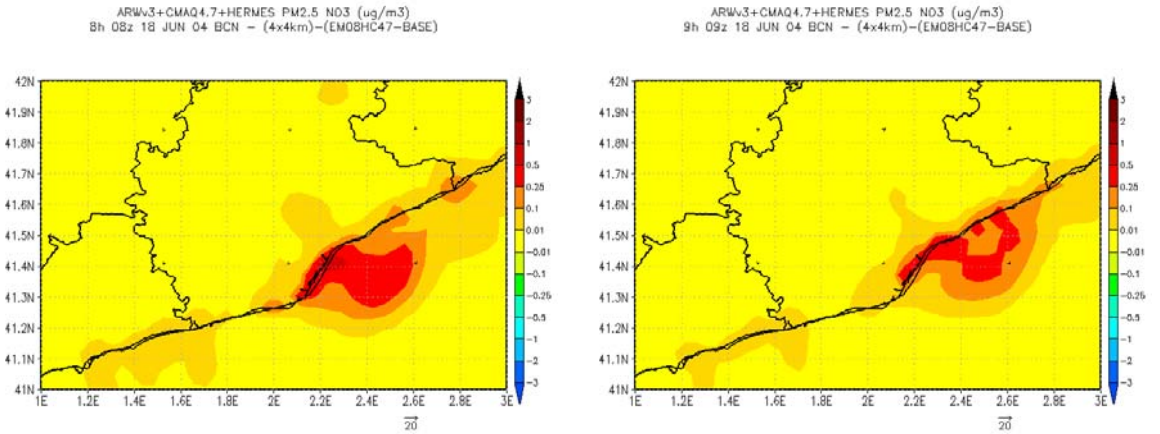
NH₄⁺

Fig. 4. PM$_{2.5}$ concentration changes in Barcelona area when introducing NO$_2$ hydrolysis on surfaces and emissions as HONO sources: EM08HC47 case respect to concentrations with only gas-phase chemistry implemented as HONO source (upper panels) at 10.00 and 11.00 h local time. Concentration changes in nitrate, secondary organic aerosols, ammonia and sulfates in the PM$_{2.5}$ fraction (lower panels) for the same case (EM08HC47 – BASE).
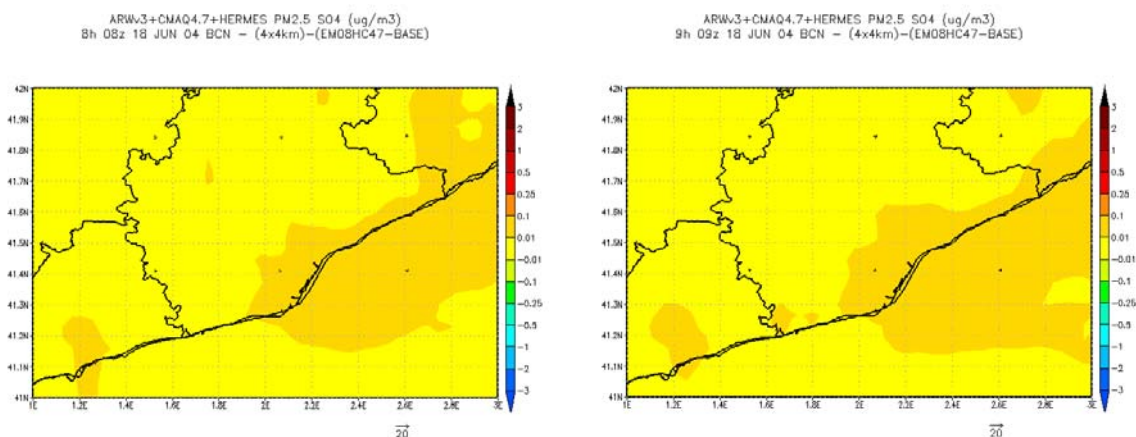
SOA
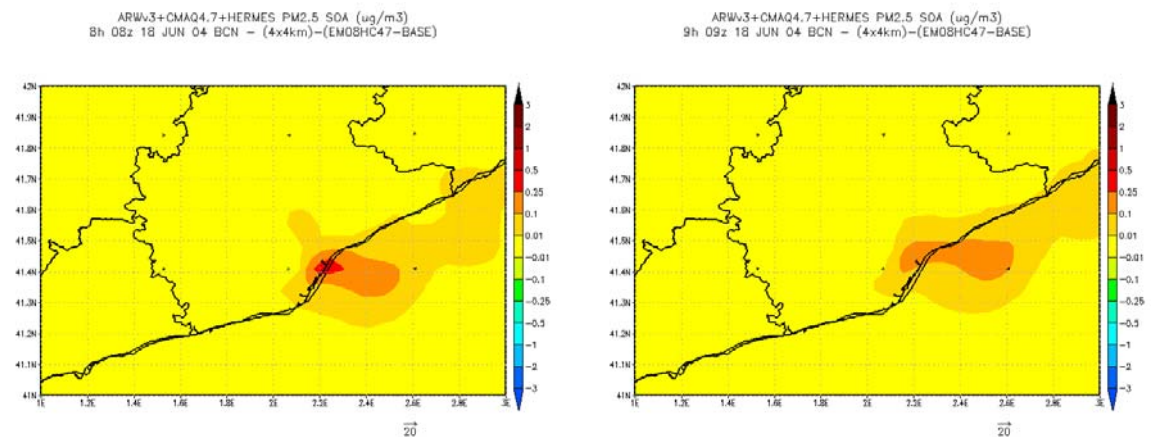
SO$_4^{2-}$

Fig. 6. Continued.

Page 28204 Statement Scattered over the Atlantic Ocean and the Mediterranean Sea, increases in chlorine aerosols are observed, which is likely to be derived from the increase of OH availability as a result of the HONO emissions from ships traffic (Fig. 9d); they are not, however, quantitatively significant compared with overall aerosol levels.

Comment: Perhaps, aerosol phase chloride or sea-salt chloride may be a better term than chlorine aerosols. Need to explain how increases in OH affect aerosol chloride?

The authors agree with Referee#2, chlorine aerosol is referred now as aerosol phase chloride. As already commented in item by item response to Referee#1's comments, CB05 contains a set of reactions considering reactive chlorine. Therefore, changes in OH concentration affect the concentration of precursors of aerosol chloride, deriving in the reported changes for this compound. Nevertheless, as stated in the manuscript, those changes are not quantitatively significant. We attribute them mainly to changes in ship emissions, which release HONO in the new cases added, resulting in the scattered variation patterns over the Mediterranean areas.

Page 28204 Statement In downwind areas from the major power plants, the increase PM$_{2.5}$ concentrations by the introduction of HONO sources is mainly produced by a change in the sulfate (SO$_4$) and ammonium (NH$_4$) levels. In Spain, there are still a number of conventional power plants that use coal as a fuel, which are important sources of sulfur oxides. In 2004, the contribution of these installations to total Sox accounted for 79% of the 1.3 kT emitted, according to the National Emissions Inventory (MARM, 2010). The sulfur oxides are precursors of sulfate aerosols, formation of which depends on the relative humidity and the oxidation capacity of the atmosphere. The release of OH in the early morning due to HONO photolysis increases SO$_4$ formation by up to 0.35 µg m^{-3} (2.9%) for the EM08HC47 case in the northern region of the Iberian Peninsula (Fig. 9e). This region is characterized by a high vegetation density (see Fig. 2a), high values of relative humidity, and concentrated agricultural activities development that act as sources of primary ammonia. The combination of these factors together with the emissions of sulfur oxides from the power plants can lead to the formation of ammonium sulfate ((NH$_4$)$_2$SO$_4$), raising both the levels of ammonia and sulfate in the aerosol phase (Fig. 9e and f).

Comment: While the gas-phase reaction of SO_2 with OH can produce sulfate, aqueous phase reaction of SO_2 with H_2O_2 is generally more significant in sulfate production. Need to explain which pathway is responsible for the increases in sulfate.

Simulations are performed using the Carbon Bond 5 chemical mechanism (Yarwood et al., 2005). CB05 includes R1 as the main reaction leading to sulfuric acid formation in the gas-phase.

$$SO_2 + OH \rightarrow H_2SO_4.$$ [R1]
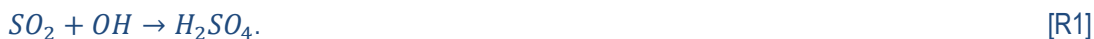
Aero5 module is used to treat the aerosols formation and interactions. Fine particles are represented by two subdivision or modes, as a function of their size: Aitken and Accumulation (Binkowski and Roselle, 2003). Conceptually, Aitken mode represents fresh particles either from nucleation or from direct emission, while the larger accumulation mode represents aged particles. The two modes interact with each other through coagulation. Each mode may grow through condensation of gaseous precursors; each mode is subject to wet and dry deposition. Finally, the smaller mode may grow into the larger mode and partially merge with it.

Sulfate aerosol in the Aitken mode can be derived from nucleation from sulfuric acid. It is estimated as a function of the production rate of sulfuric acid vapor from gas-phase oxidation of sulfur dioxide by the hydroxyl radical (R1) and the resulting mixing ratio of sulfuric acid vapor. This is the main source of secondary sulfate aerosol in the model (Binkowski and Roselle, 2003) and therefore we attribute the variations to this reaction pathway. The thermodynamic equilibrium of inorganic gas-phase species and aerosols is driven by the ISORROPIAv2.1 model (Nenes et al., 1989).

The model also considers different oxidation processes occurring in the aqueous-phase are included that could potentially form sulfate (accumulation mode), namely:

(1). Aqueous phase hydrogen peroxide oxidation reaction:

H_2O_2 + S(IV) -> S(VI) + H_2O, [R2]

(2). Aqueos phase ozone oxidation reaction:

O_3 + S(IV) -> S(VI) + O_2, [R3]

(3). Aqueous phase oxygen catalyzed by Fe^{3+} and Mn^{2+} oxidation reaction:

O_2 + S(IV) -> S(VI) [R4]

(4). Aqueous phase methyl hydrogen peroxide (MPH) oxidation reaction:

MHP + S(IV) -> S(VI) [R5]

(5). Aqueous phase peroxyacetic acid (PAA) oxidation reaction:

PAA + S(IV) -> S(VI), [R6]

R2 to R6 occur when clouds are formed (when the relative humidity reaches a value at which existing aerosol particles are activated). Those processes lead to sulfate production, but also sometimes to sulfate loss due to precipitation, etc. The simulated day, which corresponds to a typical summertime event, is characterized by low cloudiness and therefore we assume that reactions occurring in the aqueous phase are not sensitive to change sulfate aerosols concentration. The increase of OH could however raise the levels of secondary oxidants such as O_3 or H_2O_2, and therefore have an effect on the aqueous-phase chemistry.

Page 28204/28205 Statement The introduction of heterogeneous HONO chemistry results in not only changes in PM level, but also PM composition. Such phenomenon could be attributed the differences in the treatment of NO_2 uptake on ground and aerosol surfaces. The NO_2 hydrolysis on ground surfaces produces HNO_3 that is considered sticky and remains in the surfaces, not affecting further the tropospheric chemistry. In order to warrant mass conservation, this characteristic is treated through the deposition module in CMAQv4.7, being that the HNO3 productions on surfaces treated as nitrogen sinks in the first layer of the model. The same approach is not applicable, however, to the NO_2 hydrolysis on aerosol surfaces, because aerosols are distributed throughout different layers in height and not at the surface layer where deposition occurs only. Therefore, after NO_2 hydrolysis on aerosol surfaces, HNO_3 is released back into the atmosphere, leading to an increase in nitrate production. The nitrate mass increase is not quantitatively significant, but it affects the ammonia-sulfate regime. The BASENA case shows a SO_4 to NH_4 molar ratio close to 0.5 (Fig. 10) corresponding to the ammonium sulfate formation. The BASE case, which considers NO_2 hydrolysis on aerosol surfaces, shows slightly higher ratios. Ratios higher than 0.5 indicate an ammonia deficient regime and an acidic aerosol system, where the nitrate concentration is strongly dependent on ambient relative humidity (Binkowski and Roselle, 2003).

When the HONO production on aerosol surfaces is activated and HNO_3 is released (BASE), the ammonia available to react with sulfate decreases. Figure 10 (lower panels) for various urban locations suggests either the formation of ammonium bisulfate or the production of ammonium nitrate. The effect is lower in the northern region (Fig. 10, upper panels) due to the abundance of ammonia sources. A detailed analysis of the relative humidity conditions should be performed to further analyze the aerosols phase equilibrium.

Comment: This should not occur. The authors pointed out that the production of aerosol nitrate is small when the HONO production on aerosol surfaces is activated. How this small increase in aerosol nitrate affect the sulfate and ammonium needs to be clearly explained. Which specific chemistry is responsible?

In addition, Figure 10 has a scale of 0.1 mol m^{-3} for both sulfate and ammonium which translate to an unrealistically high aerosol loading in the atmosphere! Please clarify the unit used here.

Referee#2 is correct, units on the figure are (mol m^{-3})*10^{-6}, labeling is now corrected; conversion from μg m^{-3} to mol m^{-3} is made by dividing the CMAQ aerosol output concentration by the molecular mass of aerosols. Scale of Figure 10 ranges then from 0 to 0.1 10^{-6} mol m^{-3}.

The nitrate-sulfate equilibrium is governed in the aerosols module through the ISORROPIA thermodynamic equilibrium. A detailed description of such equilibrium can be found at Binkowski and Roselle (2003)[5]

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[5] Binkowski and Roselle, 2003. Models-3 Community Multiscale Air Quality (CMAQ) Model Aerosol component. Journal of Geophysical Research. VOL. 108, NO. D6, 4184, doi:10.1029/2001JD001410, 2003

Two regimes of ammonium to sulfate ionic ratio are considered. The ammonia deficient regime (in which the ionic ratio of ammonium to total sulfate ion is less than 2.0) leads to an acidic aerosol system with very low concentrations of dissolved nitrate ion which depend very strongly on ambient relative humidity. The second regime is one in which the ammonium to sulfate ratio exceeds 2.0, the sulfate is completely neutralized, and there is excess ammonia. If there is nitric acid vapor in the system, it will dissolve in the aqueous particles along with the excess ammonia and produce abundant nitrate. For cases when the relative humidity is so low that the aerosol liquid water content comprises less than 20 percent of the total aerosol mass, and the ionic ratio of ammonium to sulfate is greater than 2.0, "dry ammonium nitrate" aerosol is calculated with the following equilibrium relationship:

$$NH_4NO_3(s) \leftrightarrow NH_3(g) + HNO_3(g). \hspace{4cm} [R7]$$

In most of the analyzed cases, the ammonium to sulfate ratio in the BASENA case is close to 2.0, therefore in the limit between two different regimes: the ammonia deficient regime and the sulfate deficient regime. The HNO_3 release from the surface reaction in aerosols, in our case, could potentially lead to the formation of nitrate removing ammonia from the system, and therefore shifting the equilibrium to an ammonia deficient regime (ammonium to sulfate ratios lower than 2.0, as consistently shown in our case for the BASE case in almost all analyzed locations). Therefore even if the variation in concentration levels due to the HONO production on aerosol surfaces is low, it can affect the chemical composition of particles.

Section - Conclusions

Comment This section is too long. There is no need to repeat everything from the previous sections here. Only salient features of this study should be summarized here. Some statements based on other studies can be removed. For example, the following sentence (and many others) can be removed from the conclusion section:

The highest peak concentrations before sunrise reported up to date was 15 ppb, observed at Los Angeles in 1994, although levels reported in other locations are usually lower, ranging from 0.4 to 7 ppb.

Conclusions section summarizes now exclusively the salient features of this study, as recommended by Referee#2.

Figure 4 In addition to HONO, NO_2 is also helpful to readers. Local time is better to readers than UTC.

Figure 6 Predictions and observed data are from two different time periods; thus a fair comparison is difficult. The authors can simulate the November/December 2008 time period and compare with observed data.

Figure 9 It is difficult to read the figure; perhaps changing colors may be helpful to readers. Please explain how HONO chemistry affects chlorine. Should it be aerosol chloride, not chlorine?

Figure 10 Scale ranges up to 0.1 mol m^{-3} for both sulfate and ammonium which translate to an unrealistically high aerosol loading in the atmosphere! Please clarify the unit used here.

Comments on figures have been previously addressed; please refer to the item by item responses.