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 #1

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<u>General comments:</u>

In the model study by Gonçalves et al., sources of nitrous acid (HONO) are implemented into a 3D transport model, which was applied for the region of Spain. Different model results were compared to a base scenario, which contains only well known gas phase chemistry. In particular, two different emission scenarios and two different parameterizations of heterogeneous HONO formation by the heterogeneous disproportionation of NO_2 with water are used and compared. Since nitrous acid was shown to be a major source of primary OH radicals in recent field studies and since important HONO sources are still missing in most models, any further model development is highly recommended.

My major concerns with this manuscript are:

a)   Daytime sources:

In the manuscript, all new daytime source which have recently been discovered, for example: - HNO_3 + light: Zhou et al. (2003), - NO_2 + humic acid + light: Stemmler et al. (2006), - nitrophenol + light: Bejan et al. (2006), - NO_2^* + H_2O: Li et al. (2008), and which are necessary to explain the significant daytime levels of HONO in the atmosphere are not included or at least discussed at all. It was observed in several studies, that especially these daytime sources have the largest impact on the OH production by HONO photolysis. This was for example shown in the model study by Vogel et al. (2003), which already contained a photochemical HONO source in the model at that time. Only with this source measured daytime levels could be explained. Thus, any state of the art model should at least contain any parameterization of a daytime source.

The authors agree with Referee#1's comment, there is evidence highlighting the importance of daytime processes leading to HONO formation. Our original work focused on nighttime sources and the evaluation of their effects on HONO dynamics and secondary pollutants formation. Within such framework, emissions and heterogeneous chemistry on surfaces are the main sources of HONO (Vogel et al., 2003)[1]. However, recent works indicate that photolytic sources could contribute up to 32% in case of HNO_3 photolysis (Sarwar et al., 2008)[2], and 18% in case of NO_2 photolysis on surfaces (Li et al., 2010)[3], to diurnal HONO

[1] Vogel et al., 2003. Measured and simulated vertical profiles of nitrous acid. Part II. Model simulations and indicators for a photolytic source. Atmospheric Environment 37 (21), 2957-2966. DOI: :10.1016/S1352-2310(03)00243-7.

[2] Sarwar et al., 2008. A comparison of CMAQ HONO predictions with observations from the Northeast Oxidant and Particle Study, Atmos. Environ., 42, 5760-5770, 2008.

levels. In addition, Vogel et al. (2003)[1] clearly improve the prediction of the diurnal HONO observed levels by adding a photolytic unknown source proportional to NO_2 photolysis.

Therefore, following Referee#1′s advice, our revised work now includes a photolytic HONO source in the model. The selection of an adequate parameterization is justified in the Introduction section of the manuscript as follows:

"*Several works suggested that photoenhanced HONO formation in the atmosphere occurs over snow and on ground, vegetation, and aerosol surfaces, although the specific nature of the reaction(s) is still unclear. Zhou et al. (2003) proposed that photolysis of HNO_3 on surfaces could be a potential HONO source, and the parameterization by Sarwar et al. (2008) for this source within CMAQv4.7 model showed contributions to HONO diurnal levels of up to 32%. Nevertheless, chamber experiments questioned such a process (Kleffmann et al., 2003; Rohrer et al., 2005).*

On the other hand, Monge et al., (2010) suggested that soot provides a favorable surface for NO_2 photolysis, which can yield up to 40 ± 10 ppt h^{-1} of HONO for an atmospheric soot loading of 30 $\mu g\ m^{-3}$, and 25 ppt h^{-1} for soot deposited on surfaces, assuming typical urban values. They derive NO_2 uptake coefficients on the order of 10^{-7} to 10^{-8} depending on the initial NO_2 concentration. Stemmler et al. (2007) studied the same process on humic acid aerosols and obtained NO_2 uptake coefficients on the order of 10^{-6}. Under typical urban conditions, they estimate 17 ppt h^{-1} of HONO formation by NO_2 photolysis, concluding that this specific pathway constitutes a minor contribution to HONO ground level concentrations in the atmosphere due to low aerosols concentration. Modeling studies estimate the contribution of reactions on soot surfaces to HONO daily levels being lower than 2% (Li et al., 2010), even in highly polluted urban areas such as Mexico City. NO_2 photolysis on humic acid films, however, could be an important contributor to daytime HONO levels in the atmosphere (Stemmler et al., 2006). The proposed reaction pathway begins with the photolytic reduction of humic acid, followed by the reduced species reacting with NO_2 to yield HONO. Total photochemical production of HONO is estimated to be $5\cdot10^{10}$ molec $cm^{-2}\ s^{-1}$ for a moderately polluted atmosphere ($\approx$ 20 ppb NO_2) and solar irradiances (300-700 nm) of 400 W m^{-2}. Below such conditions the uptake coefficient for NO_2 is estimated as $2\cdot10^{-5}$. Photolysis of ortho-nitrophenols (Bejan et al., 2006) has also been shown to have a significant yield of HONO in chambers when initial concentrations of nitro-phenols are on the order of ppmv, but Li et al. (2010) demonstrated the specific contribution of this reaction to HONO levels in Mexico City is at most up to 3 ppt.

Another photolytic HONO formation pathway is through the photoelectronically excited NO_2 reaction with water in the atmosphere (Li et al., 2008; 2009).

$$NO_2^*+H_2O \rightarrow OH+HONO. \tag{R9}$$

R9 would constitute an important source of OH (directly and via HONO photolysis). However, recent experiments suggest that Li et al. (2008) results are slightly overestimated (Carl et al.,

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[3] 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.

2009), and agree with previous studies on such process (Crowley et al, 1997) in considering that the contribution of R9 is not a significant source of OH in the atmosphere (less than 2% of the production rate via O_3 photolysis). Modeling studies including this process (Wennberg and Dabdub, 2008) concluded that further investigation is needed in order to include NO_2^* reaction with water within atmospheric models.

Other modeling studies have been performed to characterize different HONO sources and quantify their impact on air quality (Moussiopoulos et al., 2000; Vogel et al., 2003; Sarwar et al., 2008; Li et al., 2010), but predicted levels of HONO have consistently been shown to be distinctively lower than values from observations."

In addition, the contributions from Gutzwiller et al. (2002)[4] and Rivera-Figueroa et al. (2003)[5] have been detailed in the revision of the state-of-the-art HONO sources in this study. Moreover, the results from Li et al. (2010)[3], which introduced the findings from Gutzwiller et al. (2002)[4] within the WRF-Chem model for Mexico City (assuming an emissions ratio of 0.023 HONO/NO_x for diesel vehicles), is compared to our high HONO/NO_x emissions ratio of 0.02 in urban areas (EM2).

Among all possible photolytic sources, the NO_2 photolysis on ground surfaces is added to our model in order to assess the effect on HONO profiles and secondary pollutants. The approach to implement this process in the CMAQv4.7 model follows the recommendations of Li et al. (2010)[3], and it is described in section 2.5 of the manuscript as follows:

"NO_2 photolysis on ground surfaces is added as a possible HONO source,

$$NO_2 \xrightarrow{h\upsilon} HONO. \hspace{5cm} (R10)$$

Kinetics are parameterized following the recommendations from Li et al. (2010) and Aumont et al. (2003), therefore the first order constant for reaction R12 is estimated via Eq. 6.

$$k_3 = \frac{1}{8} v_{NO_2} \left(\frac{S}{V}\right) \gamma_{NO_2}, \hspace{4cm} (6)$$

where v_{NO_2} is the deposition velocity of NO_2, $\left(\frac{S}{V}\right)$ is the surface to volume ratio and γ_{NO_2} is the uptake coefficient for NO_2, which is higher during daytime than nighttime in order to represent the photoenhanced HONO formation. More specifically, γ_{NO_2} is set to be $1 \cdot 10^{-6}$ for nighttime (Kurtenbach et al., 2001), $2 \cdot 10^{-5}$ for light density lower than 400 W m^{-2}, and a linearly scaled function for higher light density values, $\gamma_{NO_2} = 2 \cdot 10^{-5} \cdot \left(\frac{\text{light density}}{400}\right)$ (Li et al., 2010)."

As previously mentioned in the revised text, Li et al. (2010)[3] indicated that contribution from the reaction of NO_2 with freshly emitted soot is less than 2%, while NO_2 photolysis could contribute during daytime up to 18% of HONO. In the Iberian Peninsula, the implementation of HONO photolysis in the revisions of this

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[4] Gutzwiller et al., 2002. Significance of semivolatile diesel exhaust organics for secondary HONO formation, Environ. Sci. Tech., 36, 677-682, 2002.

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

work does not provide significant changes in HONO predicted levels, even when assessed over large urban areas, such as Madrid and Barcelona.

A detailed analysis of main differences between both studies suggests that discrepancies are due to:

1st - The surface to volume ratio parameterization

In the present work, we use a surface to volume ratio parameterization based on the land-use data. We follow the approach from Sarwar et al. (2008)[2] that consider two kinds of active surfaces: buildings and vegetation. Fig. 1 shows the estimated S/V ratio for the Iberian Peninsula during 18 June, 2004.
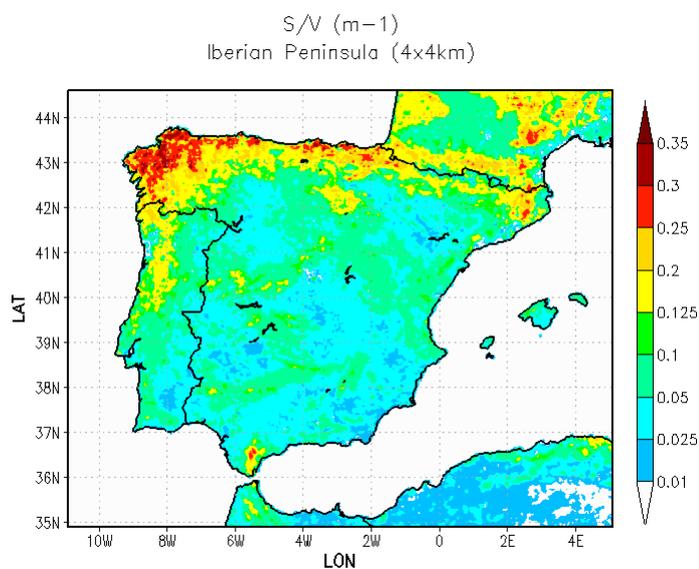

Fig. 1. Surface to volume ratios as estimated for the Iberian Peninsula for the18 June, 2004.

Vegetation surfaces are characterized as a function of the leaf area index, which in our case is derived from MODIS satellite data for June, 2004 and adapted to the Iberian Peninsula grid. The final distribution yields LAI values of up to 6.5, which is equivalent to an effective surface area of 13 m^2. However, those high values appear scattered and limited to rural regions, with low NO_x concentrations, therefore their effect on HONO production due to NO_2 photolysis is limited. The average leaf area indexes over the Iberian Peninsula are much lower than 6.5, ranging from 0.01 to 1.5, which are analogous to effective surfaces on the order of 0.02 to 3 m^2.

On the other hand, building surfaces are characterized as a function of the urban percentage in each cell. 0.2 m^{-1} is assigned for cells with 100% of urban coverage. CORINE land cover database is used to compute the urban percentage per cell in the Iberian Peninsula, resulting in urban fractions from 0 to 75%. Therefore, cells over Madrid and Barcelona urban areas have effective surfaces up to 5.7 m^2, while urban regions elsewhere in the Iberian Peninsula have effective surfaces on the order of 1.2 m^2 or lower.

The approach by Li et al. (2010)[3] and Vogel et al. (2003)[1], however, does not distinguish among different land uses when defining the surface to volume ratio. They assume an effective surface

of 1.7 m^2 homogeneously distributed over the domain, which is far below our estimates in some cases but much higher for others, depending on the reference cell.

2nd – The NO$_x$ concentrations in urban regions

Li et al. (2010)[3] report NO$_2$ concentrations in Mexico City up to 100 ppbv; Madrid and Barcelona, however, show NO$_2$ levels up to 50-60 ppbv for the studied case.

3rd – Meteorological conditions and other particularities of the studied areas

No specific data for the solar radiation hitting the ground are provided in the Li et al. (2010)[3] study. However, in the Iberian Peninsula, up to 1100 W m^{-2} of solar radiation hitting ground surfaces is estimated by WRF-ARW. These discrepancies would enhance the photolytic HONO production by a factor of 2.75.

We've also found a bug in the HCUCI cases within the CMAQ code, which has been corrected and the corresponding discussions have been updated accordingly. The corrected parameterization shows that HCUCI is less effective in producing HONO than the HC47 parameterization, even under high relative humidity conditions. The HCUCI parameterization, as well as the Li el al. (2010)[3] approaches, consider the NO$_2$ deposition velocity. We believe that this is the main reason for both the HCUCI parameterization and the new photolytic pathway to be less effective in producing HONO than the HC47 parameterization already included in the CMAQv4.7 model. Below, kinetics for HC47 reactions are implemented as Eq. 1 (Sarwar et al., 2008)[2], HCUCI equations are implemented as Eq. 2 (derived from Finlayson-Pitts et al., 2003[6]), and Eq. 3 (Li et al., 2010)[3] for the photoenhanced NO$_2$ reduction on ground surfaces, all in s^{-1}.

$$k_1 = 5 \cdot 10^{-5} \left(\frac{S}{V} \right). \tag{1}$$

$$k_2 = 9.7 \cdot 10^{-5} v_{NO_2} RH \left(\frac{S}{V} \right). \tag{2}$$

$$k_3 = \frac{1}{8} v_{NO_2} \left(\frac{S}{V} \right) \gamma_{NO_2}, \tag{3}$$

with $\gamma_{NO_2} = 1 \cdot 10^{-6}$ for nighttime (derived from Kurtenbach et al., 2001[7]) and

$$\gamma_{NO_2} = \begin{cases} 2 \cdot 10^{-5} \text{ for light density} < 400 \text{ W m}^{-2} \\ 2 \cdot 10^{-5} \cdot \left(\frac{\text{light density}}{400} \right) \text{ for light density} > 400 \text{ W m}^{-2} \end{cases}, \text{for daytime (derived from Stemmler et al., 2006[8]).}$$

v_{NO_2} represents the deposition velocity of NO$_2$ (m s^{-1}), RH, the relative humidity (%), γ_{NO_2}, the effective uptake coefficient of NO$_2$ and $\left(\frac{S}{V} \right)$ the surface to volume ratio (m^{-1}).

[6] Finalyson-Pitts et al., 2003. The heterogeneous hydrolysis of NO2 in laboratory systems and in outdoor and indoor atmospheres: An integrated mechanism. Physical Chemistry Chemical Physics 5, 223-242. DOI: 10.1039/b208564j

[7] Kurtenbach et al., 2001. Investigations of emissions and heterogeneous formation of HONO in a road traffic tunnel, Atmos. Environ., 35, 3385-3394, 2001.

[8] Stemmler et al., 2006. Photosensitized reduction of nitrogen dioxide on humic acid as a source of nitrous acid. Nature 440, 195-198. doi:10.1038/nature04603

For the same $\left(\frac{S}{V}\right)$ ratio and NO_2 concentration, Eq. [1] yields much higher HONO production than Eq. [2] and Eq. [3]. Deposition velocity of NO_2 as estimated by WRF-ARW for the 18 June, 2004, ranges from 0.0 to 4.8 x 10^{-3} m s^{-1}, with 4.4 x 10^{-4} m s^{-1} being the average for the Iberian Peninsula. Maximum deposition velocities are observed in densely vegetated areas, while urban regions are characterized by deposition values ranging from 10^{-5} to1.5 x 10^{-3}. Therefore, even for high relative humidity values (say, 100%), or maximum light density hitting the ground (say, 1100 Wm^{-2}), the values of kinetic constants from Eqs. [2] and [3] would be one and three orders of magnitude less than Eq. [1], respectively.

Further research has to be conducted to provide better characterization of available ground surfaces for reaction and kinetics parameterization of heterogeneous reactions within air quality models. Meanwhile, approaches such those that consider homogeneously distributed active surfaces in the lowest model layer, as well as others that do not account explicitly the deposition velocities to compute the constant rates, are valuable to produce HONO effectively, but they may be reproducing artificial patterns of ground concentration. Detailed implementations considering variable surface to volume ratios and the dependence of kinetics on the NO_2 deposition velocity do not produce significant changes on HONO levels, at least for moderately polluted urban areas such as those considered in the present work. Therefore further research is needed in modeling techniques that allow consideration of such variables in order to reproduce HONO observations.

However, most of the commonly used state-of-the-art modeling systems, such as Models-3/CMAQ or CHIMERE, do not include any heterogeneous photolytic source of HONO, and some of them do not account for specific emissions nor heterogeneous chemistry (e.g. the Unified EMEP model). Models provide fundamental tools to assess the effects of those additional sources on HONO levels and to explore the consequences on secondary pollutants concentration, therefore the development of new HONO sources parameterizations and test studies, as the work presented here, are highly recommended.

b)   Parameterization of the heterogeneous HONO source:

While the HONO source derived from the tunnel study of Kurtenbach et al. is correctly used, the second parameterization from the study of Finlayson-Pitts et al. is overestimated. In their table 2 and on page 238 (right column, 3. para.) a heterogeneous rate coefficient of 0.04 ppb/ppm/min for a S/V of $3.4m^{-1}$ and 50 % r.h. is mentioned, whereas a value of 0.22 ppb/ppm/min is used in the present model study. For ca. 50 % relative humidity an NO_2 uptake coefficient of 10^{-6} was derived in Kurtenbach et al., whereas values around $5x10^{-8}$ can be derived from the Finlayson-Pitts et al., study. Thus, the almost similar results for HC47 and HCUCI shown in Figure 4 are unrealistic.

The reference value for the HCUCI parameterization of the NO_2 hydrolysis kinetics, 0.22 ppb/ppm^{-1} min^{-1}, is obtained from Table 2 in Finlayson-Pitts et al. (2003)[6] by averaging all the listed measured results. This fact is stated in the manuscript, in page 28193, lines 3 to 5: *"Second, a new expression is derived using an averaged HONO production rate of previous chamber studies summarized in Finlayson-Pitts et al. (2003) for R6, 0.22 (ppb HONO) (ppm NO_2)$^{-1}$ min^{-1}"*. In addition, units of eq. [1], corresponding to Kurtenbach et al. (2001)[7] parameterization, were not properly reported in the manuscript. In (ppm HONO)(ppm NO_2)$^{-1}$ s^{-1}, k_1 value is: 5 x 10^{-5} (S/V). This aspect is now stated in the manuscript.

Furthermore, as aforementioned, an internal bug was found in the code for the HONO production calculations on the HCUCI cases, which was enhancing HONO production by a factor of one order of magnitude. This bug is now fixed and the new results show consistently lower HONO production from HCUCI parameterization than HC47 cases, even under high relative humidity conditions.

c) Intercomparison with field results:

For such a model development comparison with field measurements would be of high importance. Thus, intercomparison with some urban field data would help to validate the importance of the different sources included into the model (compare for example: Vogel et al., 2003). Such an intercomparison would help to identify missing important daytime sources (see a)) and could help to validate any humidity dependence (see below). The comparison with the field data from the study of Sörgel et al. (2010), which was derived for a different season, place, etc. (why?) is not very helpful here and in addition, the diurnal variation could not be well simulated (see below, daytime maximum).

The main goal of this work is to assess how the introduction of HONO sources in a state-of-the-art air quality model would impact model predictions. In particular, our main goal is to study the effects of those additional sources on severe pollution events. Therefore, 18 June, 2004 is selected because it corresponds to the worst air quality conditions of anthropogenic origin in the study area and it fits in a synoptic meteorological pattern representative of summer pollution events that frequently occur in the Iberian Peninsula (please refer to item by item response to Referee#2 for further details).

No HONO observations are available for the period selected, or other periods in 2004, therefore a model evaluation is not possible in terms of HONO predictions. Even if such a comparison would provide valuable information, in our opinion is not essential and it won't change the main conclusions drawn in this study.

The WRF-ARW/HERMES/CMAQ model capabilities to diagnose and forecast the air quality levels of the Iberian Peninsula have been proved elsewhere (please refer to published works as referred in the manuscript). The model performance for the selected date, 18 June 2004, has been validated as well. Model predictions for O_3, NO_2 and PM_{10} concentrations are compared to observations from ground air quality stations in the Iberian Peninsula. It is out of the scope of this work to perform a detailed model evaluation, but basic trends on the model behavior can be extracted from information on Table 1. No discrimination of air quality stations by type or area has been applied. WRF-ARW/HERMES/CMAQ slightly underestimates O_3 and NO_2 levels as reported by the air quality stations for the 18 June, 2004. PM_{10} concentrations are also underestimated, but it is unclear from the current comparison if the discrepancies are more related to natural sources, anthropogenic sources, or both. Full evaluation of the air quality model for the year 2004 trends and a deep analysis of the origins of uncertainties are presented by Baldasano et al. (2010)[9].

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[9] Baldasano et al., 2010. An annual assessment of air quality with the CALIOPE modeling system over Spain, Sci. Total Environ., submitted, 2010.

Table 1. Statistical parameters estimated for WRF-ARW/HERMES/CMAQ predictions compared to ground level concentrations of O_3, NO_2 and PM_{10} in air quality stations of the Iberian Peninsula for the 18 June 2004.

	Number of AQS	Modeled average concentration ($\mu g\ m^{-3}$) (MOD)	Observed average concentration ($\mu g\ m^{-3}$) (OBS)	BIAS ($\mu g\ m^{-3}$) (MOD-OBS)	MNBE (%) (MOD-OBS) · 100/OBS	MNGE (%) |(MOD-OBS)| · 100/OBS
O_3 (8-h ave)	68	83,6	109,6	-26,0	-17,2	30,2
NO_2 (24-h ave)	32	12,9	25,3	-12,4	-48,1	54,9
PM_{10} (24-h ave)	14	10,0	33,3	-23,3	-64,0	64,0

Since HONO observations are not available for the selected episode, the qualitative comparison with DOMINO data has been removed from the last version of the manuscript. Observations from urban areas worldwide are taken as a reference for urban HONO levels and trends (Table 3 in the manuscript).

Special comments:

Page 28184, line 7:

Lowest HONO concentrations are typically observed in the afternoon in field campaigns. A minimum "around midday" is only theoretically expected, when ignoring strong additional daytime sources.

The authors recognize the reviewer's concern with daytime sources, and agree with Referee#1 comment that some field campaigns show the minimum HONO concentrations occurring in the afternoon. However, there are still many uncertainties associated with currently available parameterizations for "strong" photolytic source of HONO, as the new simulation results incorporating daytime sources show. Also, there are other instances that observed low HONO concentrations from midday in urban areas worldwide, i.e. Los Angeles (Winer and Biermann, 1994[10]), Santiago de Chile (Elshorbany et al., 2009[11]), and Houston (Stutz et al., 2010[12]). The point of this sentence was to simply point out the trend of peaking HONO concentration occurring at nighttime, followed by a rapid decrease due to photolysis at sunrise, which then led to low concentration during midday. In order to clarify this aspect, line 7 will be rewritten as follows:

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[10] Winer, A.M., and Biermann, H.W., 1994. Long pathleng differential optical absorption spectroscopy (DOAS) measurements of gaseous HONO, NO2 and HCHO in the California South Coast Air Basin. Research in Chemistry Intermediates 20, 423-445.

[11] Elshorbany et al., 2009. Oxidation capacity of the city air of Santiago, Chile. Atmospheric Chemistry and Physics 9, 2257-2273.

[12] Stutz et al., 2010. Simultaneous DOAS and mist-chamber IC measurements of HONO in Houston, TX. Atmospheric Environment, 44 (33), 4090-4098. DOI: 10.1016/j.atmosenv.2009.02.003

"HONO observations in urban areas are characterized by high concentrations at night and drastically decrease with sunlight."

Page 28184, line 18:

Emissions should only have a relatively small impact. Typically, HONO/NO$_x$ ratios of 5% are observed under urban conditions at the end of the night, whereas only ca. 1% is directly emitted. Thus, the contribution from direct emissions to night-time HONO should be <25% and much less during daytime (other much more important source, see above).

The quantification of the contribution of different sources to HONO peak was performed for Madrid urban area accounting for HONO emissions, heterogeneous NO$_2$ hydrolysis and gas phase chemistry. In our EM2HCUCI case where HONO emissions are set as 2% of total emitted NO$_x$, 94% of the peak mixing ratio originates from direct emissions. This case represents an upper limit for our emissions parameterizations. Li et al. (2010)[3] also introduce a HONO source as 2.3% of NO$_x$ emissions based on the work of Gutzwiller et al. (2002)[4] considering the vehicle fleet composition of Mexico City. Results from Li et al. (2010)[3] showed a high (75%) HONO production contribution from emissions as well. Case EM2 is included in our model as a way to assess possible effects of a HONO sources proportional to NO$_x$ emissions, its specific nature is not discussed on the paper, but previous works suggest that a 2% emission factor is sufficient to reproduce observed HONO levels, and was recommended to the California Air Resource Board (Harley et al., 1996)[13]. The revised study simply shows that the photolytic and heterogeneous sources of HONO based on the latest parameterization methods do not present significant contributions to HONO production compared to emissions, given the meteorological and geographical characteristics within the Iberian Peninsula.

Page 28184, line 21:

Vegetation surfaces should not be a source of HONO but a sink, since effective stomatal uptake of HONO was observed for different plants in a plant chamber (Schimang et al., 2006), even in the presence of NO$_2$.

Harrison and Kitto[14] (1994) point out that vegetation surfaces could act as a source or a sink of HONO. Their results, based on field measurements, show that HONO release processes are especially important for NO$_2$ concentrations above 10 ppb, Schimang et al. (2006)[15] suggests that vegetation surfaces act mainly as a HONO sink, but their results are based on a series of experiments over four specific plant species in a tank reactor. It is beyond the scope of this work to define which approach is correct, but previous modeling studies have considered leaves as possible reaction surfaces. For example, Sarwar et

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[13] Harley, 1996. Impact of improved emissions characterization for nitrogen-containing air pollutants in the South Coast Air Basin, California Environmental Protection Agency, Air Resources Board, Research Division, Contract nº 93-310, Final report, May 1996, http://www.arb.ca.gov/research/apr/past/93-310.pdf.

[14] Harrison and Kitto, 1994. Evidence for a surface source of atmospheric nitrous acid. Atmospheric Environment 28 (6), 1089-1094, 1994.

[15] Shimang et al., 2006. Uptake of gaseous nitrous acid (HONO) by several plant species. Atmospheric Environment 40, 1324-1335, 2006.

al. (2008)[2] include ground surfaces available for reaction as a function of the percentage of urban area and the leaf area index, which is the same approach we're following in this work.

Page 28185, line 4:

The impact of the additional HONO sources on modelled ozone levels is much smaller compared to a recent model study in which measured HONO data was used (Elshorbany et al., Atmos. Environ., 2009, 43, 6398-6407), indicating the strong underestimation of the HONO source of the present model (see a).

As indicated by Referee#1, HONO levels may be underestimated in the present study. A discussion on missing sources and uncertainties regarding them is now added to the manuscript.

Nevertheless, a sensitivity analysis in terms of secondary pollutants shows that, even if underestimated, the effects of additional HONO sources are important. O_3 concentration during the morning increases up to 12 ppbv (7 ppbv) in the main urban areas due to the addition of HONO in EM2HC47 (EM08HC47), which is around 40% (20%) of the concentration in that period. Elshorbany et al. (2009)[11] reported an increase on O_3 levels up to 84% during morning hours in Santiago de Chile due to additional HONO sources. HONO levels observed at urban areas worldwide vary from 0.4 to 15 ppbv (Table 3 in the manuscript). In the case of Santiago de Chile, maximum levels of 3.7 ppbv are reported, which is higher than in cities such as Berlin, Rome, New York, Mexico City and Ontario. Therefore, a direct comparison between Elshorbany et al. (2009)[11] results for Santiago is not applicable here. On the other hand, lower increases on secondary O_3 production in the early morning, up to 7 ppbv, are found for Mexico City when adding HONO emissions, heterogeneous chemistry and photolysis (Li et al., 2010)[3] – HONO peaks measured by DOAS technique in the city range from 4 to 11 ppbv depending on the reference height.

Page 28185, line 14: The relative (. . .) importance of the HONO photolysis is not too different between urban and rural conditions. Compare for example Acker et al., 2006a (Rom) with Acker et al., 2006b (Hohenpeissenberg), but also with polar studies. In all these studies HONO is one of the most important OH sources (30-50 % of the OH sources. . .)

The authors agree with Referee#1. Here, the stress was put on urban areas for HONO photolysis due to: (1) the high concentration of other pollutants that can be oxidized by the OH release, (2) the high population density that can be affected for the pollutants. In order to clarify this aspect, we'll reword line 14 as follows: *"R1 is especially important in urban areas due to the greater potential impact OH release has in a polluted environment"*.

Page 28186, line 5:

A third order rate coefficient should not be compared to a second order rate coefficient ("20 orders of magnitude" is meaningless…). The authors agree with Referee#1. said the rate coefficient comparison has been removed in the revised manuscript.

Page 28186, line 22:

Kirchstetter. The correction is made as noted.

Page 28186, line 23-24:

The uncertainties in the HONO emissions are much lower compared to those of the other sources, see nicely refereed on page 28190: pure gasoline fleet: 0.3 % HONO/NOx, mixed fleet with diesel vehicles: 0.8 % HONO/NOx, caused by the higher HONO emissions of diesel vehicles (pure diesel: up to 2 % possible), see Kirchstetter and Kurtenbach.

Here, the authors are referring to the lack of specific data to be applied in emissions modeling when a bottom up approach is followed, i.e. HERMES-2004 traffic module considers specific speed dependent emission factors by vehicle category (depending on the fuel type, engine cubic capacity and age of the vehicle). Vehicle fleets are distributed in 72 categories according to EEA-EMEP/CORINAIR (2003)[16] methodology. Currently, the information regarding HONO emissions from traffic is still limited and it does not provide the necessary degree of detail to include this pollutant with the bottom up approach referred above. Therefore, the purpose of this paragraph was not to compare the uncertainties in emissions with the uncertainties on other HONO sources, but to indicate that more measurements must be performed in order to provide detailed emission factors for HONO as required to be applied in a bottom up approach. In order to clarify this aspect, lines 23 – 24 are rephrased as: "*In the recent decades, several studies (e.g. Kirschtetter et al., 1996; Kurtenbach et al., 2001) explored HONO emissions from on-road traffic. However, specific HONO emission factors as a function of vehicle type, fuel or speed, to be used within bottom-up emission models are not yet available.*"

Page 28187, R7:

This reaction should not only cover the NO_2 + soot reaction (Ammann et al., 1998) but is of general importance, since also other adsorbed VOCs may be a HONO source (see Arens et al., 2002; Gutzwiller et al., 2002, from the same group). Thus, R7 will be also of importance on ground surfaces containing many organics (for example: humic substances in soil, see dark experiments in Stemmler et al. (2006); but also reactions on window grime, etc.). The reactions of NO_2 with organics is typically much faster compared to the reaction of NO_2 + H_2O. E.g. in Arens et al., NO_2 uptake coefficients of 10^{-6} were derived

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[16]   EEA-EMEP/CORINAIR, 2003. Atmospheric Emission Inventory Guidebook. Technical Report 30. http://www.eea.europa.eu/publications/technical_report_2001_3

which are much higher compared to 10^{-7} - 10^{-8} for NO_2 + H_2O in smog chambers (the latter value is too slow to explain atmospheric HONO night-time formation). Thus, for the model calculation, I would leave it open whether R6 or R7 is of higher importance and just use the parameterization of Kurtenbach et al.. Also in this study only an effective heterogeneous rate coefficient could be derived for the tunnel wall substrate and the nature of the reaction was uncertain.

The Introduction has been modified in the revised manuscript in order to address the issues signaled by Referee#1. Apart from the aforementioned discussion on photolytic HONO sources, clarification on the NO_2 reduction on surfaces has been addressed as follows:

"*The reduction of NO_2 adsorbed on surfaces could also lead to nitrous acid production:*
$$NO_2 + \{C\text{-}H\}_{red} \rightarrow HONO + \{C\}_{ox} \qquad\qquad (R7)$$

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."

Page 28187, line 23:

The model calculations from Vogel et al. are missing up to here. In this study measured HONO levels could be modelled well when using state of the art (2003) HONO sources... Please refer to previous comment(s).

Page 28190, line 9:

Jenkin et al. is a model study in which theoretical HONO/NO_x factions of 0-0.05 were implemented into a model and thus, this reference should not be used in this context ("using different vehicles and engine tests... "). The reference has been removed in the revised manuscript.

Page 28190, line 25:

The used NO_2/NO_x ratio of 5 % for on road traffic is not state of the art. Recent measurements in many European studies have shown increasing ratios up to ca. 25 % depending on the fleet composition (typically: 0.15).

The 5% ratio is obtained from the EEA-EMEP/CORINAIR methodology (2003)[16] for the estimation of atmospheric emissions. The most recently updated guidelines (EEA-EMEP/CORINAIR, 2009[17]) suggest values of NO_2/NO_x ratio from 2% to 25% for vehicles up to Euro III. The lowest ratios, up to 5%, are assigned to gasoline fleets, which constitute 52% of the total vehicle fleet for Spain in 2004. The highest ratios, 25% NO_2/NO_x, correspond to Euro III diesel vehicles, which account for 18% of the vehicle fleet in HERMES-2004 inventory. Therefore, the NO_2/NO_x ratio may be slightly underestimated in HERMES-2004 inventory, but differences on total emissions should not be significant.

Page 28191, line 15:

". . . involving NO_2 and water. . ." should be reaction R6? Or NO_2+NO+water? Next sentence: reaction R3 can be neglected also based on field experiments, in which night-time HONO formation was observed without NO present.

R6 is the heterogeneous hydrolysis of NO_2, therefore it is not included in the gas-phase chemistry discussed in section 2.3. CB4 and CB05 include a reaction of NO_x and water ($NO+NO_2+H_2O$), while CACM considers exclusively NO_2+H_2O. This aspect has been clarified in the updated version of the manuscript. Also, a comment on the HONO formation without NO present is now included.

Page 28192, line 4:

Stutz et al. is not a tunnel or chamber study. . . The reference has been removed from the original manuscript.

Page 28192, line 6:

Vegetation surfaces should not be used see above. . . As aforementioned, vegetation surfaces are parameterized for NO_2 hydrolysis following the approach of Sarwar et al. (2008)[2].

Page 28192, line 24:

A S/V of 0.2 m^{-1} is quite high? For example, even for a very low BLH of 100 m, S/V will be 0.01 m^{-1}. Even considering vertical walls this should not increase the S/V by a factor of 20. Pores of any wall substrates should not be included here, since this has already been included in the parameterization of Kurtenbach et al. (they used geometric uptake coefficients). What is the height of the lowest layer in the model?

The reference value is obtained from the last release of the CMAQ model and supported by Sarwar et al. (2008)[2] and it is weighted considering the urban coverage fraction for each 4x4 km^2 cell. Vertical sigma levels are used within CMAQ. Therefore, the lowest layer height depends on the surface pressure. At atmospheric pressure on the surface, the height of the lowest layer in the model is 38 m. Vogel et al. (2003)[1] and Li et al. (2010)[3] consider an effective surface of 1.7 m^2 per geometric surface in the lowest layer of their model. Our parameterization for surface to volume ratios gives higher effective surfaces for some cells in the domain and lower for others (please refer to 1st general comment response for details).

Page 28197, line 5:

What is a "false peak"? Specify the time shift, magnitude etc.

Predicted maximum HONO levels in the BASENA and BASE cases are found between 800 and 1200 hours UTC. While these peak values are low (100 pptv for rural locations or 300 ppt for urban areas), HONO daily profile is expected to show a maximum before sunrise and to decrease rapidly due to photolysis after sunrise. Hence, the noon-time peak is referred to as a "false peak", and such behavior is observed in the model when only gas-phase chemistry is included. Additional sources of HONO have to be considered in order to reproduce the HONO build-up during nighttime (as shown in Figure 4 when emissions or heterogeneous chemistry is added). This paragraph is reworded in order to clarify these aspects as follows:

"Moreover, HONO peak in the BASENA case is predicted in the early morning, and not before sunrise as expected (Fig. 4), due to the lack of HONO sources to represent the HONO buildup during nighttime. This behavior has also been observed in previous works that use CMAQv4.6 with CB05 chemical mechanism (Sarwar et al., 2008). Since the most commonly used chemical mechanisms share the same basic reactions related to HONO gas-phase sources and sinks (Table 1), models using exclusively HONO gas-phase chemistry are likely to predict analogous daytime false-peaks. Therefore, additional sources must be included within air quality models in order to capture observed levels."

Page 28198, line 24:

Whether the humidity is a "key factor" in the heterogeneous NO$_2$ conversion or not is still under discussion and cannot be deduced from the present study (higher variability is no argument, as long as validated by intercomparsion with field data. . .). In addition, from Figure 4, I do not see too large differences between the HC47 and HCUIC model runs, which are also not expected here (most is direct emission in the model, thus small impact of a small variability in the heterogeneous source. . .). Thus, by far not a "key factor" here. The humidity dependence from the study of Finlayson-Pitts et al. (2003) was determined for ppm NO$_2$ experiments. However, for much lower atmospheric NO$_2$ levels (see Kleffmann et al., 1998), no humidity dependence was observed. For R7, which is expected to be of higher importance (including the ground, see above. . .), the humidity dependence is even more complex than simply linear (see for

example the soot reaction in Kalberer et al., 1999). HONO formation may even decrease with humidity, see also recent field results for very high humidity.

Corrected HCUCI parameterizations yields much lower HONO production than HC47, even for high relative humidity values. Therefore, conclusion on the relative humidity effect has been removed in the revised the manuscript. Nevertheless, the authors still believe that RH should be included in the parameterizations for deriving NO_2 hydrolysis kinetics, as it is a factor with a high temporal and geographical variability. Finlayson-Pitts et al. (2003)[11] experiments were performed with NO_2 concentrations higher than atmospheric levels, but Stutz et al. (2004)[18] also showed a linear dependence of HONO/NO_2 ratio on RH during nighttime by means of field measurements, thus confirming the necessity of including RH dependence in modeling studies. Observational studies by Qin et al., (2009)[19] supported the theory that RH has to be considered within the NO_2 heterogeneous conversion to HONO as well. There's still certain controversy on the effects of RH on the NO_2 hydrolysis kinetics for high RH values (above 80%), therefore as stated by Referee#1, further research must be conducted in order to assess the specific dependence on RH.

Soot reactions (e.g. Kalberer et al., 1999)[20] are not added in this work, apart from the parameterization already included in CMAQv4.7 model. The reason being even if the formation rate of HONO seems to be fast in the first minute of exposure to NO_2, the passivation of soot surfaces slows down the formation afterwards.

Page 28199 sec. para. – 28200, comparison with Sörgel et al.:

The model data shown in Fig. 6 is highly interesting, since all model scenarios show a clear daytime maximum of HONO, which should be caused here by R2 (no other daytime source included. . .). This maximum is in nice agreement with daytime maxima often observed under rural conditions (see for example, Acker et al., 2006/Hohenpeisenberg). However, for rural conditions, for which the night-time HONO levels are lower than 100 ppt (see Fig. 6), the daytime NO levels should be extremely low. Thus, reaction R2 can typically only explain a few ppt of HONO at maximum under these conditions. Accordingly, the maximum in the model results is unclear here and it seems that the daytime NO is too high and constant in the model, but should not be.

Fig. 2(a) shows the evolution of NO concentration in the El Arenosillo station, as estimated by WRF-ARW/HERMES/CMAQ model for the 18 June, 2004. Daytime NO levels remain low as expected for rural areas. NO peaks in the early morning, achieving up to 0.5 ppbv (6.1 µg m^{-3}), which is potentially attributed to the influence of the ships emissions from the Strait of Gibraltar (see supplementary materials),and the industrial area located at a distance of 20 km away, as discussed in the original manuscript. However, the

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[18] Stutz et al., 2004. Relative humidity dependence of HONO chemistry in urban areas. Journal of Geophysical Research 109, D03307, doi:10.1029/2003JD004135.

[19] Qin et al., 2009. An observational study of the HONO-NO2 coupling at an urban site in Guangzhou City, South China. Atmospheric Environment 43(36), 5731-5742. doi:10.1016/j.atmosenv.2009.08.017

[20] Kalbereret al., 1999. Heterogeneous Formation of Nitrous Acid (HONO) on Soot Aerosol Particles, J. Geophys. Res., 104, 13 825–13 832, 1999.

qualitative comparison of HONO predictions with observations for El Arenosillo station has been removed from the last version of the manuscript, as previously justified.
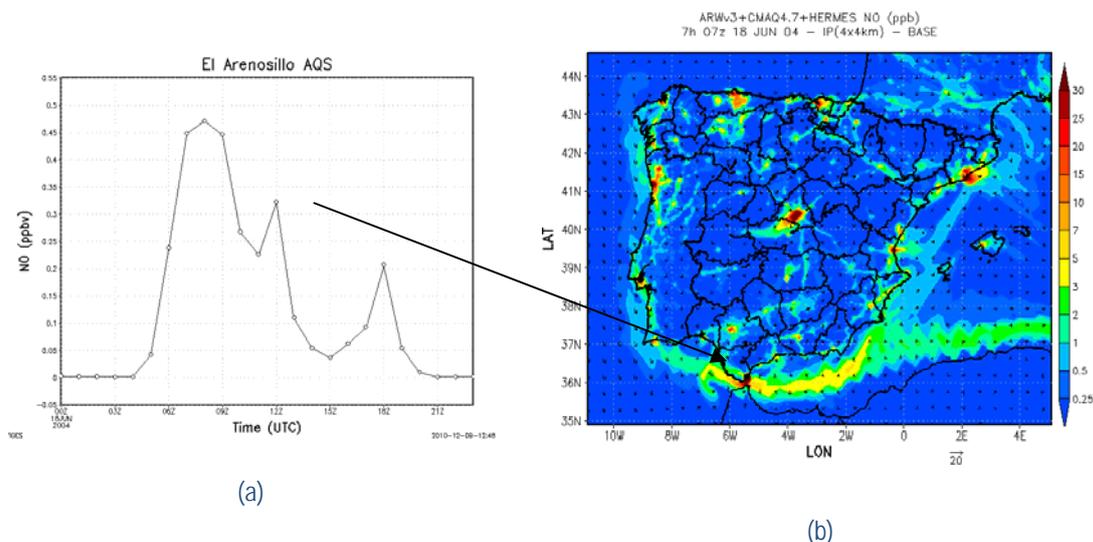

(a)

(b)

Fig. 2. (a) Hourly evolution of NO concentration (ppbv) in the BASE case during the 18 June, 2004 in the location of the El Arenosillo Air Quality Station (AQS). (b) NO concentration (ppb) in the Iberian Peninsula at 700 UTC as estimated by means of WRF-ARW/HERMES/CMAQ model for the BASE case (arrow indicates approx. location of El Arenosillo AQS)

Page 28202, line 8:

Changes of 1-5 % of ozone peak concentrations are much lower than expected when using measured daytime HONO (see above) and are clearly in between the errors of any model ("quite significant").

As discussed before, the most significant changes are observed in O_3 levels in the early morning (up to 40%, depending on the scenario). Even changes from 1% to 5% in O_3 peak are considered significant because of their effect on human health and the interest for modelers to predict peak concentrations accurately (2008/50/EC European Directive sets thresholds for population information and alert for O_3 hourly levels). Moreover, the 2008/50/EC directive indicates that O_3 model predictions are accepted for management purposes while model uncertainty remains below 50% when compared to observations. The WRF-ARW/HERMES/CMAQ modeling system fits within the European and the US-EPA recommendations to be used for management purposes.

Changes in O_3 peak of around 4 ppbv are observed in downwind areas from the main NO_x sources in the Iberian Peninsula when additional HONO sources such as emissions, photolytic processes, and heterogeneous chemistry are added. These results are in agreement with Aumont et al. (2003)[21], who reported 4 ppbv increases in O_3 peak for a summertime polluted day when introducing heterogeneous chemistry and emissions in a box model.

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[21] Aumont et al., 2003. Contribution of HONO sources to the NOx/HOx/O3 chemistry in the polluted boundary layer. Atmospheric Environment 37, 487-498.

Page 28202, line 19:

"after sunrise": using a more realistic HONO chemistry this sentence would change (see above. . .).

HONO observations in urban areas show a peak before sunrise (see references from Table 3 in the manuscript), therefore HONO photolysis (and subsequent OH release) is expected to peak after sunrise. In our case, maximum changes in secondary pollutants concentrations due to HONO addition occur in the early morning (together with main changes on OH release). Those findings are in agreement with modeling results in other areas, where largest impacts due to HONO sources addition also occur in the early morning (e.g. Elshorbany et al., 2009; Li et al., 2010)[11,3]. Even if additional diurnal sources of HONO were included in the model, changes in OH budget are expected to peak in the early morning; therefore our conclusion would still be valid.

Page 28204, line 1:

What is a "chlorine aerosol" ? Cl^- containing aerosol? And why should this increase (mostly caused by sea spray. . .)?

Chlorine aerosol refers to the amount of chlorine ion present in the aerosol phase as estimated by the CMAQ model. This term is changed in the revised manuscript to aerosol chloride. The Carbon Bond 5 mechanism used in this study includes a reactive chlorine mechanism (Yarwood et al., 2005)[22] of 21 reactions, which involve interactions among Cl_2, VOCs, NO_x and O_3. Those reactions may be indirectly influenced by HONO release, deriving in slightly higher concentrations of HCl. Aero5 module used in this study includes a chemically interactive coarse particle mode that enables dynamic transfer of HNO_3, H_2SO_4, HCl, and NH_3 between coarse particles and the gas phase (Kelly et al., 2010)[23]

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[22] Yarwood et al., 2005. Updates to the Carbon Bond Chemical Mechanism: CB05 Final Report RT-04-00675. December, 8, 2005. 246 pp. (on http://www.camx.com/publ/, August, 2009)

[23] Kelly et al., 2010. Simulating emission and chemical evolution of coarse sea-salt particles in the Community Multiscale Air Quality (CMAQ) model, Geoscience Model Development 3, 257-273, doi:10.5194/gmd-3-257-2010.