

## ***Interactive comment 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**

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The impact of different nitrous acid sources in the air quality levels of the Iberian Peninsula

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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

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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.

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.

Section 2.1 – Modeling framework Page 28189 Statement After a thorough analysis of O<sub>3</sub>, NO<sub>2</sub> and PM<sub>2.5</sub> 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 too 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.

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 Environ-

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mental 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 NO<sub>x</sub>. CMAQv47 (which the authors used here) considers HONO from on-road motor vehicles and uses 0.8% of NO<sub>x</sub> as HONO.

More information can be found at: [www.epa.gov/ttn/chief/emch/index.html#2005](http://www.epa.gov/ttn/chief/emch/index.html#2005). Specific file: [ftp://ftp.epa.gov/EmisInventory/2005v4/ancillary\\_smoke/ancillary\\_2005v4\\_smokeformat](ftp://ftp.epa.gov/EmisInventory/2005v4/ancillary_smoke/ancillary_2005v4_smokeformat).

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<sub>x</sub>. Currently, the recommendation from the US-EPA allocates 95% of total NO<sub>x</sub> as NO and 5% as NO<sub>2</sub> for on-road traffic emissions, and 90% as NO and 10% as NO<sub>2</sub> for all other sources.

Comment: This is old. Currently, USEPA uses 90% of NO<sub>x</sub> as NO and 10% of NO<sub>x</sub> as NO<sub>2</sub> for all sources except motor vehicles which uses 90% as NO, 9.2% as NO<sub>2</sub>, and 0.8% as HONO.

More information can be found at: [www.epa.gov/ttn/chief/emch/index.html#2005](http://www.epa.gov/ttn/chief/emch/index.html#2005). Specific file: [ftp://ftp.epa.gov/EmisInventory/2005v4/ancillary\\_smoke/ancillary\\_2005v4\\_smokeformat](ftp://ftp.epa.gov/EmisInventory/2005v4/ancillary_smoke/ancillary_2005v4_smokeformat).

Statement In order to include HONO emissions two different emissions parameterizations are examined in this work: (1) 0.8% of NO<sub>x</sub> from mobile sources, the most widely accepted HONO/NO<sub>x</sub> emission ratio; (2) 2% of total NO<sub>x</sub> 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 NO<sub>x</sub> speciation. If 0.8% of NO<sub>x</sub> from mobile sources are taken as HONO, how the remaining (99.2%) NO<sub>x</sub> emissions are speciated into NO and NO<sub>2</sub>. Is NO or NO<sub>2</sub> adjusted for mass conservation? Similarly, if 2% of

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total NO<sub>x</sub> for all the anthropogenic sources are taken as HONO, how the remaining (98%) NO<sub>x</sub> emissions are speciated into NO and NO<sub>2</sub>. Is NO or NO<sub>2</sub> adjusted for mass conservation?

Additionally, 2% of total NO<sub>x</sub> 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 NO<sub>x</sub> 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.

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<sub>2</sub> 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<sub>2</sub>(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 NO<sub>x</sub> 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<sub>3</sub> can react with NO to produce HONO. Zhou et al (2003) suggested HONO production from adsorption of HNO<sub>3</sub> on ground. Bejan et al (2006) suggested HONO production from the photolysis of nitrophenol. Stemmler et al. (2006, 2007) suggested that NO<sub>2</sub> can potentially

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react with humic acid to produce HONO. Li et al. (2008, 2009) suggested that excited NO<sub>2</sub> 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-NO<sub>x</sub> 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. Phys.*, 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 NO<sub>2</sub> and H<sub>2</sub>O, *Science* 319, 1657-1660.

Li, et al, 2009. Response to comment on atmospheric hydroxyl radical production from electronically excited NO<sub>2</sub> and H<sub>2</sub>O, *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.

Section 3.1 – Air quality levels in the Liberian 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 O<sub>3</sub> above 100 ppb from 14:00 to 16:00UTC (Fig. 3a).

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Comment: Local times are easier for readers than UTC.

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.

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.

Page 28198 Statement The HC47 parameterization for the NO<sub>2</sub> 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

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HCUCI parameterization (Fig. 5). Therefore relative humidity is a key factor to be considered in the parameterization of the kinetics of the NO<sub>2</sub> 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.

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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 NO<sub>x</sub> and HONO emissions in Iberian Peninsula should also be presented.

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.

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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.

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.

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<sub>2</sub> formation. NO<sub>2</sub> 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<sub>2</sub> profile will be helpful to readers. As pointed out earlier, HONO is produced at the expense of NO<sub>2</sub>. Thus, when HONO emissions are estimated, NO<sub>2</sub> emissions should be reduced; otherwise total nitrogen species will not be conserved. Similarly, when HONO production from heterogeneous reactions is considered, NO<sub>2</sub> should be reduced to account for the production of HONO and consumption of NO<sub>2</sub>.

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.

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### Section 3.4 Impacts of additional HONO sources on the secondary PM2.5

Page 28203 Statement The increase in PM2.5 levels in urban areas is mostly attributed to changes in nitrates (NO<sub>3</sub>) 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 NO<sub>x</sub> levels from traffic emissions are likely to further oxidize and yield nitric acid (HNO<sub>3</sub>). Gas phase HNO<sub>3</sub> 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  $\mu\text{g m}^{-3}$  (14%) and 0.65  $\mu\text{g m}^{-3}$  (13%) in the EM08HC47 and EM08HCUCI cases are found (Fig. 9b).

Comment: Increases in PM2.5 levels have been attributed to the increases in nitrate and SOA. Nitrate goes up by a maximum of 0.7  $\mu\text{g m}^{-3}$  and SOA goes up by up 0.35  $\mu\text{g m}^{-3}$ . However, PM2.5 increases by up to 3.0  $\mu\text{g m}^{-3}$ . Need to explain the cause of the additional increases in PM2.5.

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?

Page 28204 Statement In downwind areas from the major power plants, the increase PM2.5 concentrations by the introduction of HONO sources is mainly produced by a change in the sulfate (SO<sub>4</sub>) and ammonium (NH<sub>4</sub>) 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 SO<sub>x</sub> accounted for 79% of the 1.3 kT emitted, according to the National Emissions Inventory

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(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<sub>4</sub> formation by up to 0.35  $\mu\text{g m}^{-3}$  (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<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>), raising both the levels of ammonia and sulfate in the aerosol phase (Fig. 9e and f).

Comment: While the gas-phase reaction of SO<sub>2</sub> with OH can produce sulfate, aqueous phase reaction of SO<sub>2</sub> with H<sub>2</sub>O<sub>2</sub> is generally more significant in sulfate production. Need to explain which pathway is responsible for the increases in sulfate.

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<sub>2</sub> uptake on ground and aerosol surfaces. The NO<sub>2</sub> hydrolysis on ground surfaces produces HNO<sub>3</sub> 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 HNO<sub>3</sub> productions on surfaces treated as nitrogen sinks in the first layer of the model. The same approach is not applicable, however, to the NO<sub>2</sub> 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<sub>2</sub> hydrolysis on aerosol surfaces, HNO<sub>3</sub> 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<sub>4</sub> to NH<sub>4</sub> molar ratio close to 0.5, (Fig. 10) corresponding to the ammonium sulfate formation. The BASE case, which considers NO<sub>2</sub> hydrolysis

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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<sub>3</sub> 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<sup>-3</sup> for both sulfate and ammonium which translate to an unrealistically high aerosol loading in the atmosphere! Please clarify the unit used here.

Section 3.4 Impacts of additional HONO sources on the secondary PM<sub>2.5</sub>

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.

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Figure 4 In addition to HONO, NO<sub>2</sub> 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<sup>-3</sup> for both sulfate and ammonium which translate to an unrealistically high aerosol loading in the atmosphere! Please clarify the unit used here.

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

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