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Atmospheric Chemistry and Physics Discussions

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

Anonymous Referee #1

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General comments:

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 parameterisations of heterogeneous HONO formation by the heterogeneous disproportionation of NO2 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:

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a) Daytime sources: In the manuscript, all new daytime source which have recently been discovered, for example: -HNO3 + light: Zhou et al. (2003), - NO2 + humic acid + light: Stemmler et al. (2006), - nitrophenol + light: Bejan et al. (2006), - NO2* + H2O: 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.

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 NO2 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.

c) Intercomparison with field results: For such a model development comparison with field measurements would be of high importance. Thus, intercomparion 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

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well simulated (see below, daytime maximum).

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.

Page 28184, line 18:

Emissions should only have a relatively small impact. Typically, HONO/NOx 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).

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 NO2.

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).

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.,

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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. . .).

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. . .).

Page 28186, line 22:

Kirchstetter

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.

Page 28187, R7:

This reaction should not only cover the NO2+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 NO2 with organics is typically much faster compared to the reaction of NO2+H2O. E.g. in Arens et al., NO2 uptake coefficients of 10-6 were derived which are much higher compared to 10-7 - 10-8 for NO2+H2O 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

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wall substrate and the nature of the reaction was uncertain.

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...

Page 28190, line 9:

Jenkin et al. is a model study in which theoretical HONO/NOx 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. . .").

Page 28190, line 25:

The used NO2/NOx 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).

Page 28191, line 15:

". . . involving NO2 and water. . ." should be reaction R6? Or NO2+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.

Page 28192, line 4:

Stutz et al. is not a tunnel or chamber study. . .

Page 28192, line 6:

Vegetation surfaces should not be used see above. . .

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

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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?

Page 28197, line 5:

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

Page 28198, line 24:

Whether the humidity is a “key factor” in the heterogeneous NO2 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 NO2 experiments. However, for much lower atmospheric NO2 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.

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

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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.

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").

Page 28202, line 19:

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

Page 28204, line 1:

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

Page 28205, line 2:

HNO3 formed by reaction R6 on particles is not expected to be released to the atmosphere (high Henry's law coefficient).

Page 28205, line 4:

How can the NO2+H2O reaction on particles influence the ammonia-sulfate regine? This reaction should be not of importance compared to the uptake by gas phase HNO3 and the N2O5 hydrolysis on particles (e.g. gamma(HNO3) ca. 0.01 compared to gamma(NO2) ca. 10-6 – 10-7).

Some errors in the references:

Alicke et al, 2003: Pätz, H.-W., Schäfer, Ammann et. al.1998: Rössler, Gäggler, Bejan

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et al., 2006: Bejan, I., Abd et Aal, Y., Check others. . .

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