Atmos. Chem. Phys. Discuss., 12, C4027–C4032, 2012
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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Impact of HONO on global atmospheric chemistry calculated with an empirical parameterization in the EMAC model" *by* Y. F. Elshorbany et al.

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Received and published: 26 June 2012

General remarks:

In the paper by Elshorbany et al. different parameterizations were used in a global model to describe more realistically the impact of nitrous acid (HONO) on the oxidation capacity of the atmosphere. This is of high importance since many recent field and accompanying model studies demonstrated the significant importance of HONO on the HOx budget of the atmosphere. Although some reasonable results were obtained and although the parameterizations used are a significant improvement of current global models, I have several general comments to the manuscript.

1) HONO/NOx ratio:

While an average daytime HONO/NOx ratio of 2 % may be quite reasonable (although the peaking behaviour often observed during early afternoon, see figure 1, is lost than. . .), the similar number used for the night-time is too low. This has been demonstrated in many field campaigns (up to 20 % HONO/NOx often observed) and can be also seen from figure 1, for which almost all night-time data is >2 %. In addition, the use of a constant HONO/NOx ratio makes no sense caused by the increasing HONO/NOx ratio during night-time (see again figure 1). So if a simple parameterization is used, why not using the linear increase of the HONO/NO2 ratio, described by a simple first order rate coefficient (k(NO2-HONO)) as pioneered in the study by Alicke et al., 2002 and as shown in the model study by Vogel et al., 2003? For this rate coefficient very similar values (around few times 10ˆ6 sˆ-1) were published in many field studies (including the Santiago studies by Elshorbany et al. and see attached Figure 1). In addition, during daytime still a constant HONO/NOx ratio may be used.

2) Logarithmic dependence of HONO/NOx on NOx:

The decreasing HONO/NOx ratio with increasing NOx is quite interesting and has been observed in many field studies (compare e.g. urban and remote studies). On page 12895 this is explained by heterogeneous formation of HONO, which is said to be confirmed by the wind speed dependency shown in Figure 4. However, this section is not clear for me:

a)If heterogeneous HONO formation is first order in NO2 as typically observed in the laboratory, the HONO/NOx ratio should be independent on NOx. Thus, the more reasonable explanation for that observation is a first order (in NO2) formation process of HONO and a second order (in HONO) loss reaction of HONO, typically observed for heterogeneous HONO decomposition on different surfaces. I.e. at low HONO, the decomposition is less effective compared to high HONO (and NOx) levels, leading to higher HONO/NOx ratio at lower pollution levels.

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b)The wind speed dependency of the HONO/NOx ratio shown in Figure 4 would be in contradiction with a surface source (in opposite to the statement) and is also in contradiction with the wind speed dependency of the night-time HONO formation observed during the Santiago summer campaign by Elshorbany et al.. For that campaign the night-time HONO formation was inversely decreasing (. . .) with increasing wind speed (see attached Figure 1) in opposite to the linear positive dependency shown here. For a very reasonable night-time formation on ground surfaces (see e.g. Kleffmann et al., 2003) as proposed also here, increasing wind speed will lead to higher turbulent mixing of the surface layer, leading to a lower effective S/V and to lower effective rate coefficients for heterogeneous HONO formation on ground surfaces in line with the Santiago summer results. Thus, the positive linear dependency observed here is hard to explain by a ground surface source and may be accidentally caused by the choice of campaigns.

3) Negative correlation of the unidentified HONO source with the actinic flux:

In Figure 9 a negative correlation of the unidentified HONO source with J(NO2) and J(O1D) is shown. This is hard to understand and again in contradiction with the results from several recent field studies including the Santiago studies by Elshorbany et al., for which a positive correlation was observed. The latter is quite reasonable in context to the proposed photochemical sources. The unreasonable dependency shown in Figure 9 is simply caused by the choice of campaigns. Whereas the summer HOxCOMP campaign (high actinic flux) was under quite clean conditions (low absolute HONO source. . .) the Santiago winter campaign (lower actinic flux) was under extremely polluted conditions (stronger source. . .). The same holds when comparing Santiago winter with summer (different pollution levels). So here apples and oranges are compared, implying that the source would be decreasing with increasing actinic flux, which will be not the case. So if these campaigns should be directly compared in one diagram, the data has to be normalized to the different pollution levels, e.g. by dividing with the NOx precursor levels. Thus, also several comments in the text on that point should be

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modified. E.g. the paragraph on the bottom of page 12900 and the top of the following page needs to be re-written (the observation is surprising!). In addition, while the temperature dependence explanation given there may be partially reasonable (at lower T, lower BLH, higher S/V ratio and thus more effective formation) the J(NO2) and J(O1D) artificial anti-correlation is unreasonable (see above) and by definition not in line with any night-time results from Veitel and Febo.

Minor concerns:

1) Page 12887, lines 22-24:

The different sources identified in the laboratory can explain ground based measurements as shown e.g. in studies by Zhou et al. for rural and Stemmler et al. for urban conditions and as also mentioned in Elshorbany et al., 2010b. The problem not mentioned here is that these sources can not explain the small gradients recently observed in the mixed boundary layer (Zhang et al, 2009, Häseler et al., 2009).

2) Page 12896, lines 13-16:

As demonstrated in a recent study by Villena et al. (J. Geophys. Res., 2011, 116, D00R07) the HONO source strength of the daytime source can be proportional to the NO2 concentration even in the remote atmosphere, in contrast when only the HONO levels are considered (which did not correlate to NOx in that study in agreement with other remote studies). In addition, the statement given in line 16 is in contradiction with figure 9, which clearly shows that the daytime source of HONO depends on the pollution (NOx precursor) level (s. discussion above).

3) Page 12897, lines 4-5:

In contrast to the given statement, emissions can significantly contribute to the HONO levels in the urban atmosphere, as shown in the study by Vogel et al., 2003. In addition, if a 2% HONO/NOx ratio is considered here, than emissions with a typical HONO/NOx ratio of 0.8 % (see Kurtenbach et al., 2001 and see also Elshorbany et al., 2009) may

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contribute by 40 %.

4) Page 12903, lines 19-20:

From Figure 12 it appears that the reality lies between the S2 and S3 runs, which mean that the used 2 % HONO/NOx may be too low, especially during night-time.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 12885, 2012.

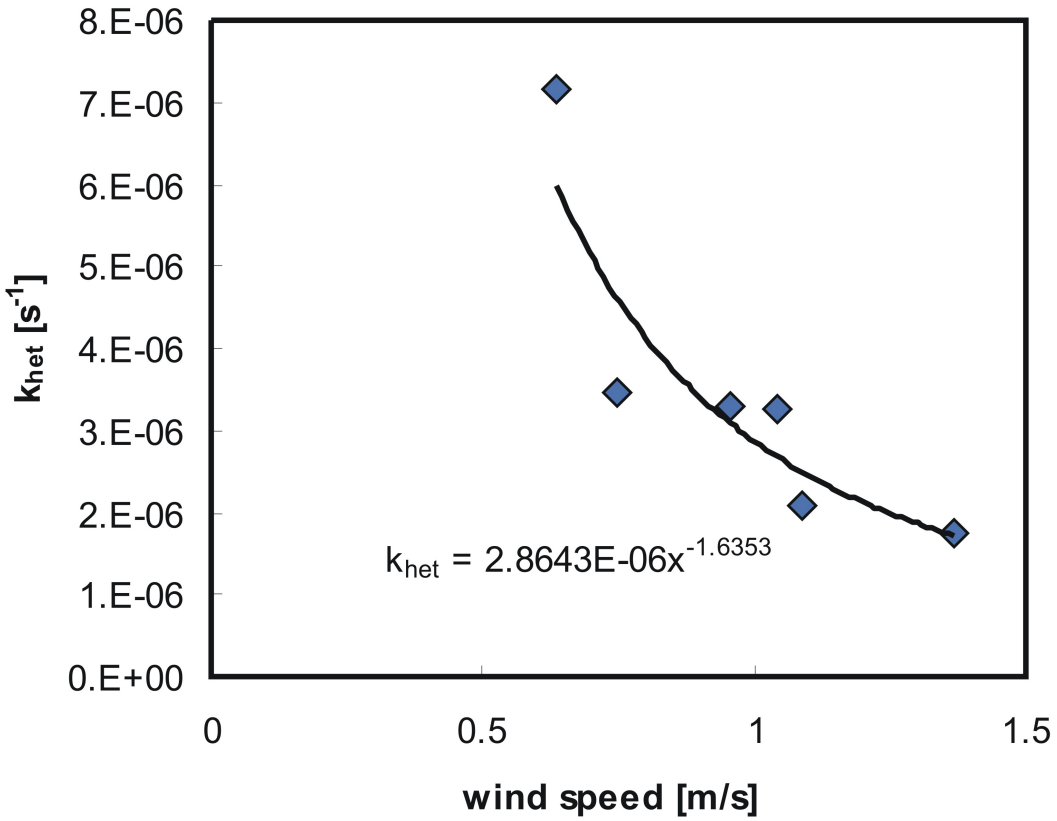

Fig. 1.

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