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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Modeling nitrous acid and its impact on ozone and hydroxyl radical during the Texas Air Quality Study 2006" *by* B. H. Czader et al.

B. H. Czader et al.

bczader@UH.edu

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Thank you for reviewing the manuscript. Please find reply to your comments below.

- In the introduction (Section 2.1) different sources of HONO are discussed but most of the newer (field) work is not referred to: Li et al. ACP 2012; Wong et al. ACP 2012; Wojtal et al. ACP 2011; Sörgel et al ACP 2011; Yu et al. ACP 2012; Su et al. Science 2011. It might not be necessary to discuss these in detail. However, these provide additional views on the potential HONO sources which should be mentioned.

(Reply) Thank you for pointing to these latest literatures on HONO. We included these in the paper, but listed them in the second paragraph of the introduction together with

other literature to provide the general overview. Section 2.1 is meant to describe HONO sources that are taken into account in the simulations. Regarding the Yu el al. ACP 2012 paper that you have mentioned, we found one entitled "Decreasing particle number concentrations in a warming atmosphere and implications" but it does not provide any insights on HONO. There is another Yu el al. ACP 2009 entitled "Observations of high rates of NO2-HONO conversion in the nocturnal atmospheric boundary layer in Kathmandu, Nepal", did you have this one in mind? If not please let us know the DOI number of the Yu paper we should refer to.

- The current manuscript tries to address a number of questions: HONO profiles, HONO sources, and the HONO impact on OH and ozone. It contains four time series of HONO and of NO2 but the profiles are not thoroughly analyzed. The statement "CMAQ could be validated successfully against vertical resolved HONO measurements" in the Conclusions is not clear from the presented model-data comparison. If the authors want to address the profile question I suggest a much more detailed analysis of HONO and NO2 profiles. In this case, the result of this analysis should also be mentioned in the abstract. However, the paper by Stutz et al. (2010) already showed that there is excellent agreement between DOAS and MC/IC. When looking at the discussion on the sources, I am not convinced that all different HONO, NO2, and O3 time series are required to make the statements of this work. Finally, the discussion on the impact of HONO (based on Figures 5, 8, and 9) refers to one day only not being representative for the measurement period.

(Reply) We believe that the strength of presenting time series for different altitudes rather than profiles is that they actually provide information on individual hourly data, which may otherwise get lost, if merged into average profiles. Showing individual profiles based on hourly data would result in very busy plots. The statement: "CMAQ could be validated successfully against vertical resolved HONO measurements" is based on the comparison of measured and simulated HONO mixing ratios at different heights and on the following discussion in section 3.1: "While daytime measurements show

only slight dependence with altitude, HONO mixing ratios at night and early morning decrease with altitude, with maximum values reaching about 2 ppbv at the low level and only about 0.5 ppbv at the upper level. Contrary to the measured values, HONO mixing ratios from the G case do not show variation with height. HONO values obtained from GEH and GEHP cases correctly capture the trend towards lower nighttime and early morning mixing ratios at higher altitudes. In addition, including photolytic HONO sources in the GEHP case resulted in average 100 ppt higher daytime HONO concentrations at the low DOAS level and an average daytime increase of 50 and 30 ppt at the middle and upper DOAS levels, respectively." These results are also mentioned in the abstract.

(Reply) The reason we concentrated on Aug. 31 is that it was one of the two days in 2006 with the poorest air quality index for Houston (see also Rappenglück et al., 2008). A peak 8-hr average of 126 ppbv was measured at one site in the Houston area. Also, meteorological modeling (Ngan et al., 2012) has been extensively studied. We thought that it may be of highest priority to analyze the potential impact of HONO on O3 formation on O3 exceedance days and avoided to look into days with moderate or background O3 levels. Such a justification is added to the manuscript (first paragraph of section 3.2). However, to provide a more complete picture of this specific episode we now extended the OH time series (now in figure 4) to show 31 Aug. – 2 Sep.; figure 8 was extended to show in addition a comparison for 30 August. Figure 9 has already presented results for Aug. 30 – Sep. 1. Also, O3 time series in Figure 7 were removed for DOAS middle and upper levels.

Ngan, F., D. W. Byun, H. C. Kim, B. Rappenglueck and Pour-Biazar, A.: Performance Assessment of Retrospective Meteorological Inputs for Use in Air Quality Modeling during TexAQS 2006. Atmos. Environ., 54, 86-96, doi:10.1016/j.atmosenv.2012.01.035, 2012.

Rappenglück B., R. Perna, S. Zhong, G.A. Morris, 2008: An Analysis of the Vertical Structure of the Atmosphere and the Upper-Level Meteorology and their Im-

pact on Surface Ozone Levels in Houston, Texas, J. Geophys. Res., 113, D17315, doi:10.1029/2007JD009745

- Specific comments:

- What is the purpose of Figure 2? The information is not used in the remainder of the discussion. The discussion based on Figures 5, 8, and 9 is one day only.

(Reply) The purpose of figure 2 is to clearly show differences in simulated HONO mixing ratio obtained with different cases. It was prepared because it is difficult to capture those differences from HONO time series. Additional explanation was added to the manuscript (3rd paragraph in section 3.1).

(Reply) Regarding analysis for one day see comments above.

- The paragraph on the measurement-model comparison (page 5859) at different altitudes is difficult to follow, since only time series are presented in the Figures 3 and 4. As already stated above an analysis of the altitude profiles needs different figures. Even though it would be nice to have a better analysis of the HONO profile issue, it might not be required for the interpretation of the HONO sources and impact here.

(Reply) We believe that that the strength of presenting time series is that they provide information on individual hourly data as opposed to snapshots in profile figures or merged into average profiles (see also previous comments above).

- The authors analysed one day with OH measurements only which was selected for the good fit between model and measurements. In my opinion this cannot be accepted as a criterium: 1. Other days show similar good agreement. 2. 31 Aug 2006 is the highest HONO peak and not representative for the measurement period.

(Reply) OH measurements are only available for couple of days during the episode of interest. We have extended the comparison to Aug. 31 – Sep. 2 (see also previous comments made above).

Technical corrections:

- Time and dates formats are mixed. Use dd MMM [yyyy] and 24-h time in the entire manuscript and for all figures.

- Explain IRR analysis.

- Figure 1 caption should note measurement altitude MC/IC.

- Please merge Figures 1 and 3. Mention the measurement altitude of MC/IC in the figure caption or legend. See also General comments.

- Figure 5 has different time axes. Merge in panels using one time axis.

- The three panels of Figure 9 should merge onto one page with one time axis. Please label HONO as ppb in the Figure.

(Reply) All technical corrections have been addressed in the revised manuscript. The explanation of IRR analysis has been added to the second paragraph of section 2.

(Reply) Regarding Figure 5, it is now split into two: figure 4 which presents OH time-series for 31 Aug. - 2 September, and Figure 5 (proviusly Figure 5b) that shows IRR results for 31 August.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 5851, 2012.

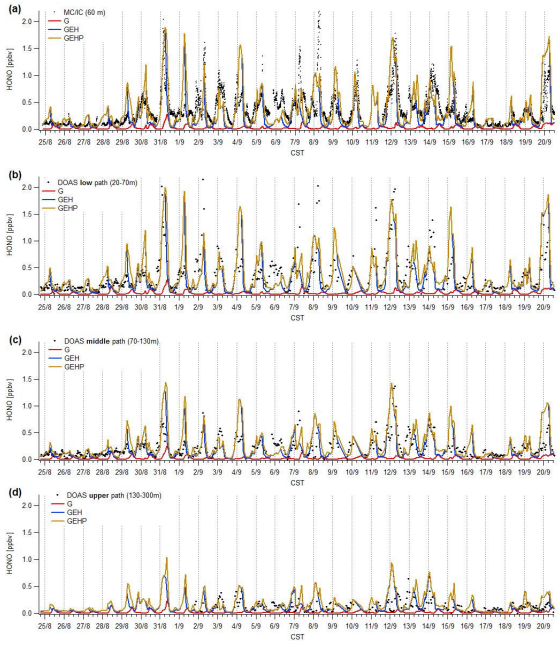

Fig. 1.

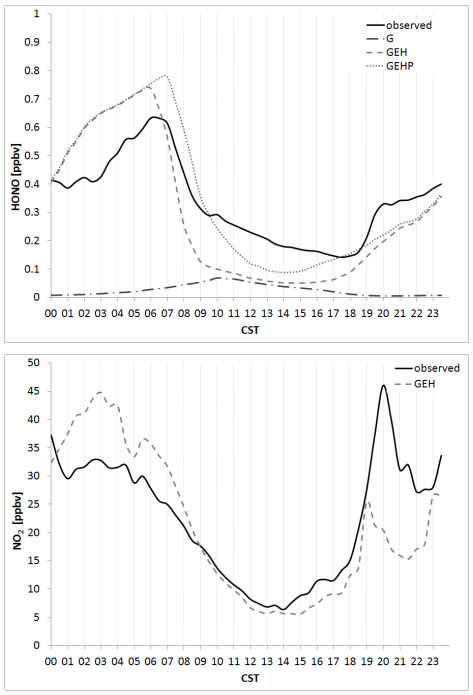
observed
G
GEH
GEHP
HONO [ppbv]
CST
observed
GEH
NO2 [ppbv]
CST

Fig. 2.

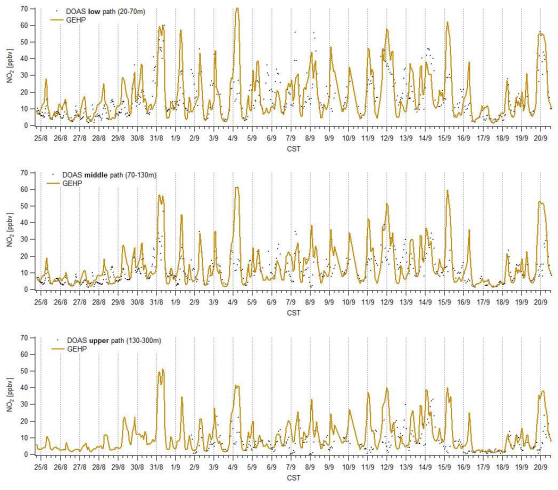
DOAS low path (20-70m)
GEHP
DOAS middle path (70-130m)
GEHP
DOAS upper path (130-300m)
GEHP
CST

Fig. 3.

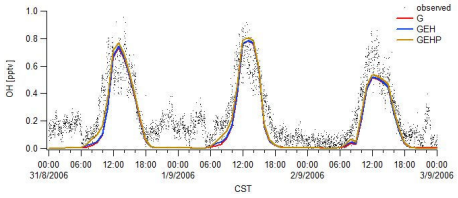
observed
G
GEH
GEHP
OH [pptv]
1.0
0.8
0.6
0.4
0.2
0.0
00:00 06:00 12:00 18:00 00:00 06:00 12:00 18:00 00:00 06:00 12:00 18:00 00:00
31/8/2006
1/9/2006
2/9/2006
3/9/2006
CST

Fig. 4.

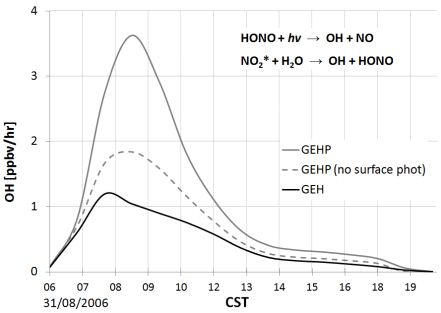
HONO + hν → OH + NO
NO2* + H2O → OH + HONO
GEHP
GEHP (no surface phot)
GEH
OH [ppbv/hr]
4
3
2
1
0
06 07 08 09 10 12 13 14 15 16 18 19
31/08/2006
CST

Fig. 5.

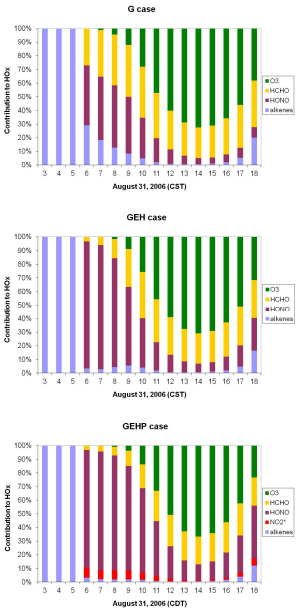
G case
GEH case
GEHP case
Contribution to HOx
August 31, 2006 (CST)
August 31, 2006 (CDT)
O3
HCHO
HONO
NO2*
alkenes

Fig. 6.

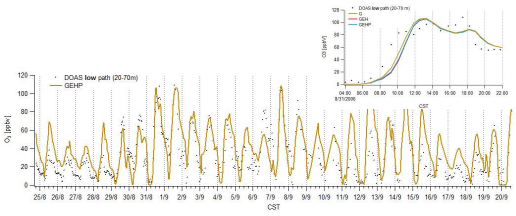
DOAS low path (20-70m)
GEHP
CST

Fig. 7.

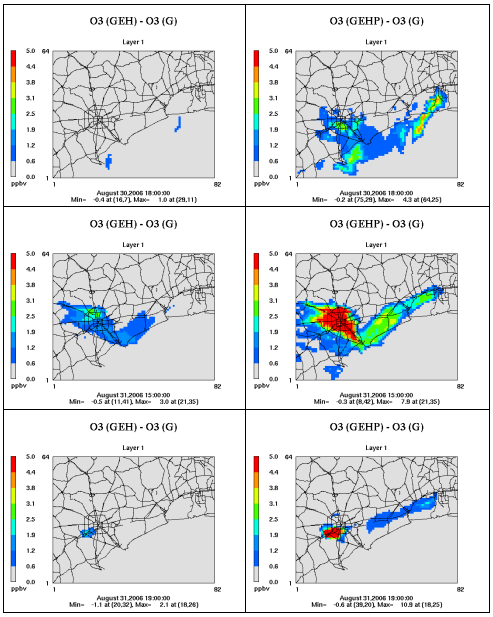
O3 (GEH) - O3 (G)
O3 (GEHP) - O3 (G)
Layer 1
ppbv

Fig. 8.

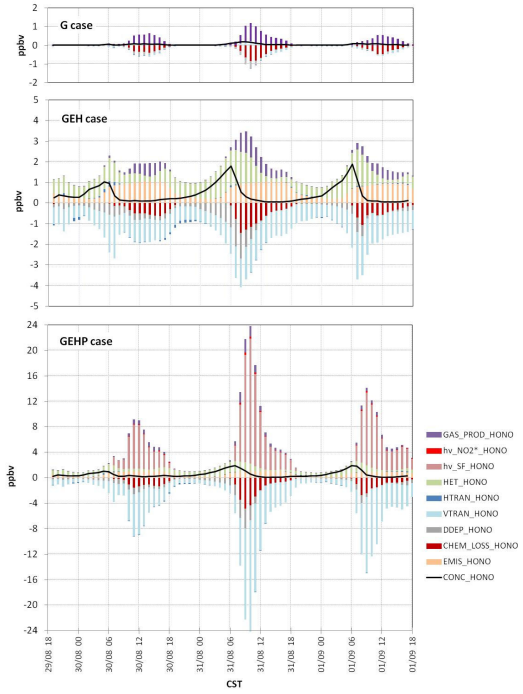
G case
GEH case
GEHP case
ppbv
CST
GAS_PROD_HONO
hv_NO2*_HONO
hv_SF_HONO
HET_HONO
HTRAN_HONO
VTRAN_HONO
DDEP_HONO
CHEM_LOSS_HONO
EMIS_HONO
CONC_HONO

Fig. 9.