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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Measurements of HONO during BAQS-Met" *by* J. J. B. Wentzell et al.

Anonymous Referee #2

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Comment on "Measurements of HONO during BAQS-Met" (Wintzell et al.)

This paper presents approximately 3 weeks of HONO measurements made in a semi-rural location just north of lake Erie (i.e., in a region surrounded by a variety of urban and industrial centers of activity). The data appear to be of high quality and quite interesting. A key finding is that daytime levels remain substantial despite the short lifetime against photolysis, presumably due to strong production throughout the day by unknown heterogeneous processes. Both the observation of unexpectedly high day-time HONO and attribution of it to strong heterogeneous production have now become common features of reports on HONO (in urban and rural settings).

The authors explore whether production of HONO from photolyticly excited NO2 might be a strong enough daytime source to sustain the persistence of HONO that was observed. I find that the steps in the analysis are not very clearly described, and may

not be conceptually sound. Further, I am confused by statements in the abstract and conclusion that appear to contradict each other. Specifically, last line of abstract simply reports a wide range of apparent rate constants for this possible source reaction, while conclusions note that such a range of rate constants is not plausible for a gas phase reaction therefore implicating heterogeneous processes. I note that the statement in conclusions also seems to follow from the discussion in sections 4.1 and 4.2 and the fact that the estimated rate constants (tabulated in Table 3) greatly exceed rates measured in the laboratory. However, section 4.1 points out that there is large range in the rates reported from lab studies but makes no comment on whether the much faster rates reported by Li et al. should be discounted. I note that the slopes in Figures 7 - 10 yield apparent rates that range just 2- to 7-fold higher than derived by Li, and, as pointed out by referee #1, the estimated HONO production rates (calculated by rearranging equation 1) actually include production from all sources and should be reduced by known or estimated sources other than the photolyticly excited NO2 path (e.g., NO + OH, heterogeneous production, possibly NO2 and EC, NO2 with organics, etc.). Properly accounting for these other sources would lower the slopes, hence apparent rate constants, and perhaps bring them into statistical agreement with Li et al (not likely to make them small enough to agree with Crowley and Carl or Carr et al.)

I also found the discussion through section 3, meant to be leading up to need to explore excited NO2 as a daytime source, convoluted. In section 3.1 a more or less steady increase in HONO/NO2 from 0.5 - 4.0% over 4 hours early in the night of 23/24 June is used to estimate conversion rate. Here it is noted that the rate is comparable to similar estimates in several urban areas, but clearly too slow to sustain 10's of pptv of HONO against photolysis during the daytime. In second paragraph of section 3.0 it is pointed out that this particular night was somewhat unusual, in that HONO concentrations stopped increasing around midnight, perhaps due to strong heterogeneous production from NO2 on wet grass being balanced by deposition of HONO to the same wet grass. That may be a valid explanation, but does it not also make it difficult to assert that the estimated production rate on this particular evening should be considered representative of the entire campaign?

In section 3.3 I think the authors also use the estimate derived from these 4 hours in the evening of 23 June as the rate for heterogeneous production of HONO from NO2 during the daytime. If wet grass dominated the production on this night, how could that be suggested as a rate likely to prevail for all daylight hours? On a larger "style" point, I find that section 3.3 up through line 13 on page 15304 takes a long time to make a very well established point, e.g., daytime sinks of HONO are so strong that well established sources can not account for mixing ratios greater than a few pptv. In fact, this point was made quite directly previously in the last sentence of section 3.1. Granted, the authors want to extend the steady analysis in the following section, but equation 1 could be introduced more directly.

Editorial suggestions

Pg 15300 lines 9-11 How were the daytime and nighttime intervals defined? Precise sunrise and set, threshold actinic flux levels, set times close to sunrise and set?

Line 21, callout should be Figure 2

15301, 21 "boundary layer"

15302, 26 not clear what is meant by "both cases"

15303, 2-4 Disagree with assertion that HONO/NO2 >5% were not seen in daytime when winds came from S and S/W, both by looking at the plot and reading statement on previous page that max values of the ratio in daytime observed when winds were 180-270

18-25, when describing ther terms in equation 1 it would seem more clear to define first the sources, then the sinks, rather than alternating between them

15304, 6 How was HONOpss calculated (estimated) when NO was < 1 ppb (detection limit)? How often was this a problem? (See your own comment (15300, 20) regarding

quality of NO data.)

15319 caption describes a top and bottom panel, my version shows left and right. I am pretty sure the left one is daytime.

15320-15323 captions for all of these plots are confusing, probably wrong. I think the Y axes are calculated production rates, X axes are the product of estimated excited NO2 times water vapor (not a production rate)

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 15295, 2010.