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Interactive comment on "NH_3-promoted hydrolysis of NO_2 induces explosive growth in HONO" *by* Wanyun Xu et al.

Anonymous Referee #2

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The paper "NH3-promoted hydrolysis of NO2 induces explosive growth in HONO" by Wanyun Xu et al is joining the long series of scientific work aiming at elucidating the HONO sources that have been published these past twenty years. Considering the major role of HONO in the initiation of the photo-oxidation cycles in the troposphere, any significant work related to the processes that give birth to this key molecule are necessarily important (Kleffmann et al, 2007).

Wanyun Xu et al are mostly founding the exploitation of their results on a methodology based on recent papers only and are often disregarding the precious findings of the early times. Nevertheless, they provide here an attempt to exploits a limited set of data obtained in heavily polluted environment that is not without any merit.

Overall, I have many minor points to discuss but, for me, one major point is shining

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Discussion paper

a doubtful light over the whole study: it concerns the reliability of the HONO/NO2-measurements themselves. The reliable measurement of HONO at low level in the atmosphere has been an analytical challenge for decades. Many groups have worked on various analytical concepts ranging from long path spectroscopy, optical cavities, ionic chromatography or dye formation combined with absorption within waveguide tubing or HPLC analysis...

Because of HONO high reactivity the risk of underestimation of its concentration is often high. In the same time, because of the multiplicity of its heterogeneous sources the risk of positive artefact and unwanted HONO generation in/nearby the system is high too. This is why, even when the measurement principle itself was mature, the sampling condition was often found to be a key parameter for trustable measurements which has led to important work on the design of inlets, minimizing surfaces, choosing material. . .

Each of these instrumental concept has required extensive characterization works and a few inter-comparison exercises have demonstrated how large the discrepancies can be (Keuken et al, 1990; Stutz et al, 2009; Kleffmann et al, 2006; Pinto et al, 2014).

In the present paper, the whole experimental strategy relies on the performance of the so-called In situ Gas and Aerosol Compositions Monitor (IGAC, Fortelice International Co.,Taiwan) as both HONO/NO2- and NH3 concentrations – the two key species of the present study - are monitored using this instrument. The available information about this device are scarce: IGAC consists in a combination of a wet annular denuder and a particle into liquid sampler. Unfortunately it has been poorly characterized in general and none of the reference provided in the paper are relevant for HONO measurements. In particular, while citing Liu et al, 2017a to claim “the instrument has shown good performance in the past” or quoting Young et al, 2016, one can only regret that nothing in these papers really concern nitrous acid or nitrite ions measurements. Further, Young et al, 2016 indicate that the performance of IGAC were poor concerning the measurement of ammonia.

On my side, considering the IGAC experimental device and condition of use, I especially worry about the use of “a dilute H2O2 solution to collect the gases”. If one refer to Young et al, 2016 the “dilute solution” is a 5x10-3 M solution (why not mentioning the concentration in the experimental section?) which is used to “assure the oxidation of SO2 to SO4– and prevents microbial growth “. For me, it is highly probable that such a concentration of such a strong oxidation agent could induced artefacts in the HONO measurement: - in the absence of precursors, it may induce a negative artefact by oxidizing nitrites to nitrates but, on the contrary - in the presence of enough reduced nitrogenous species (such as ammonia) it may forms HONO. In this case this would both affect NH3 and HONO measurements and would probably lead to a correlation between both species (if ammonia is in excess).

Considering the poor level of details provided in the experimental section, the lack characterization experiments demonstrating the ability of IGAC to measure HONO (especially in the presence of ammonia) and the strong suspicion of artefacts exactly relevant from the main paper conclusion, I strongly recommend to provide the experimental evidences that demonstrate the suitability of the measurement protocol for both NH3 and HONO before considering any publication.

Other Major issues

Line 213-214: “The O3 concentration stayed near zero, which means that UV radiation was weak.” This statement is clearly wrong. From the few NO data that the author disclose to the reader one can see that NO values are typically ranging from 20 to 100 ppb. With such high values, no wonder why O3 remain low: it is clearly titrated by NO. One can understand that the lack of spectral radiometer measurements is an issue (see later) but O3 data in a polluted environment can certainly not be used as a proxy for UV radiation strength.

Line 226: Equation 1 is strongly oversimplified.

On the HONO sinks side one clearly miss - photolysis that can certainly not be ne-

glected. Even if radiation measurements are not available, the authors manage, later on in the paper, to evaluate some values that could be used here. Another approach would be to provide an upper limit evaluating the J value above haze using TUV for example (see Madronich et al, 1988 and Tie et al, 2003) - deposition can be taken into account by using as deposition velocity the value given by Stutz et al., 2002, for example. In addition in the presence of hydrometeors, one clearly miss the loss processes onto/into haze droplets. On the HONO source side, may well identified processes are missing such as direct emission and heterogeneous HONO formation from conversion of NO2 on ground surface and aerosol surfaces.

Line 304-306 then line 326-329: In these section the photolysis of HONO is described being rapid (which is probably true) while it has been neglected earlier. I think the manuscript need reorganization to discuss more coherently the photochemistry of HONO under these conditions.

Minor issues

Figure 2: it is somewhat disturbing that the figure does not displayed all the data acquired. In particular (but not only) the absence of NO and ozone data is clearly a problem. Furthermore, the use of "ppb" for aerosol composition is confusing: is it related to the whole volume of air? Is it related to the whole aerosol quantity. Please use more straightforward units here.

Line 98 – 108: The experimental description of the instrument, the inlet and the protocol is insufficient.

Line 120: The authors indicate the use of a NOx monitor 42CTL from thermo. It is not clear if this instrument is equipped with a Mo-based converter, a Blue light converter or both. In any case, the risk of interferences with HONO on the NO2 and NOx channels are high (through the conversion of HONO on heated Mo – see Dunlea et al, 2007 for example - or through its photolysis by the blue light. During some part of this field campaign the HONO values can be as high as 20 % of NO2. In this case it would be

necessary to evaluate the cross-sensitivities of NO2 and HONO in the configuration of the chemiluminescence monitor used.

Line 127: “wavelength” is misspelled

Line 229: The value of 10ˆ6 radicals/cm3 is taken as “typical for noontime haze condition” and later used in the equation 1. Even if the order of magnitude of this guess is probably not too wrong there is no reference provided. Furthermore, I don’t think that the scientific community have the necessary background to raise a “typical value” for these quite peculiar conditions. I would rather recommend to refer to published work such as Whalley et al, 2015 (field) or Tie et al, 2003 (large scale modeling)

Line 267-269: This statement is quite vague. Which anions are the authors referring to ? More explanation are needed.

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