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Reply on RC2

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Author comment on "A source for the continuous generation of pure and quantifiable HONO mixtures" by Guillermo Villena and Jörg Kleffmann, Atmos. Meas. Tech. Discuss., https://doi.org/10.5194/amt-2021-332-AC2, 2021

Reply to Anonymous Referee #1

The manuscript "A Source for the Continuous Generation of Pure and Quantifiable HONO Mixtures'' by Villena et al. reports the setup and the characterizations of a continuous source generating pure HONO mixtures. The manuscript is well organized and provides valuable information which is quite helpful for performing accurate HONO measurement. I recommend the publication. And only some minor comments follows.

We would like to thank referee #1 for her/his interest and helpful comments, which will improve the quality of the paper.

1. Line 81, Page 3: Would the 99.999% pure liquid nitrogen contain some NOx and contribute to the NOx formation of the HONO source?

Answer: Since the used gas phase nitrogen was produced by evaporation of liquid nitrogen "5.0" (99.999 % purity) at the liquid nitrogen tank of the chemistry department and transferred to the laboratory by the central nitrogen feed line, the purity of the gas phase should be significantly better than 99.999 %, since most impurities (especially any NO_2 as HONO precursor) should remain in the liquid phase at the low temperatures (77 K) during the evaporation. In addition, from our experience with the purity of compressed nitrogen gas from the same manufacturer, we did not yet observe any measurable NO_x impurities, excluding significant additional HONO formation.

2. Line 87, Page 3: The generated gaseous HONO is guided to measurement instrument through PFA line. What about the wall loss of HONO on the line? It would be helpful if the authors provide a recommendation on the maximum length of the guiding line.

Answer: Especially at low HONO levels we observed a significant tailing of the signals (see Figure 3), which we attributed to adsorption of HONO on the surfaces behind the HONO source. However, from the experiment shown in Figure 3 we conclude that most adsorption took place on the stainless-steel and filter surfaces of the inlet of the chemiluminescence instrument, but not on the PFA transfer lines used. At the end of the experiment shown in Figure 3, the source was first switched to water (at 16:09), which should make the HONO source to a perfect "zero-gas generator" after a short time.

However, after a first fast decrease of the HONO mixing ratio (logarithmic scale…), there was a significant tailing of the signal at lower HONO levels. We think that this tailing does not results from the HONO source or the PFA surfaces behind the source, as the slope of the decreasing HONO levels did not significantly changed, when the HONO source was physically disconnected and the chemiluminescence instrument was operated by pure nitrogen (at 16:59). Possibly, HONO adsorbed on the inlet particle filter or on the stainless-steel inlet surfaces of the instrument is still desorbing to the gas phase even after longer time. This was also the reason, why the time response of the source slightly increased with decreasing HONO levels. In contrast, we do not think that HONO losses by adsorption on PFA surfaces is a significant problem. In former unpublished experiments with the HONO source at a smog chamber the exchange of a 3 m long PFA-line (4 mm i.d., 2 L/min) by a 20 m long one did not change the measured HONO levels, even at low ppb levels.

With respect to a similar comment by referee #2 we have added the following information to section 3.2, where Figure 3 is explained: "The increasing time response at low HONO levels is explained by adsorption/desorption of HONO on the surfaces behind the HONO source, which gets less important with increasing HONO levels, leading to faster saturation of the surfaces. From the experiment shown in Figure 3, we conclude that most of this adsorption/desorption took place on the surfaces of the chemiluminescence instrument used (inlet particle filter, stainless-steel lines) and not on the PFA transfer lines. At 16:09 the HONO source was switched from reagents to pure water, for which the HONO emissions should quickly decrease to zero. However, after a first fast decrease of the HONO concentration there was a significant tailing of the signal. Here the slope of the decreasing signal did not change when the HONO source was replaced by pure nitrogen at 16:59. This can only be explained when the tailing is caused by desorption of HONO from the surfaces of the chemiluminescence instrument, as all other PFA surfaces were removed. This conclusion is also in agreement with our experience with pure HONO mixtures, for which adsorption losses in PFA transfer lines of up to 20 m length were found insignificant."

3. Line 179 - 181, Page 6: Please add in the figure caption what the error bars represent for. The same for other figure captions in the manuscript.

Answer: The y-error bars in Figure 2 represent the precision errors (2 σ), which are only visible for the NO_x/HONO data, but smaller than the size of the symbols for HONO and NO_y. The x-error bars represent the accuracy of the pH, which was estimated to ±0.2 for pH<2, ±0.15 for pH 2-3 and ±0.1 for pH >3, caused by the problems with the pH measurements at higher acidity, see main text. In the revised manuscript all error bars will be explained in the figure captions.

4. Line 184 - 188, Page 6: Please note that the time response indicated by Figure 3 should also contain that of the chemiluminescence instrument.

Answer: Yes, we agree, most probably the decreasing time response of the source at lower HONO levels is caused by adsorption/desorption on the inlet surfaces of the chemiluminescence instrument, which will be explained in detail in the revised manuscript, see our response to point 2.

5. Figure 3, Page 7: Concerning the stronger fluctuation of NOy signal observed at lower

nitrite concentrations, does it caused by the measurement sensitivity not good enough or by the HONO source not stable under such condition?

Answer: The noise of the HONO signal at low levels will be caused by the noise of the chemiluminescence instrument. Have in mind that the HONO signal is calculated from the difference of the signals of NO_y and two times of NO, leading to corresponding higher noise of the calculated HONO data compared to the measured NO. In addition, the visually high noise at low concentrations is also caused by the logarithmic scale of the Figure. In contrast, there is no reason, why the emission of the HONO source should get more variable at lower HONO concentrations, since nothing (gas and liquid flow rates, mixing of the reagents, etc.) except the nitrite concentration was changed in the experiment.

6. Section 3.6, Page 9: The stability of the HONO source is given by a 2σ relative error. Does it mean that the stability depends on the generated HONO concentration? However, when look at Figure 3, the fluctuation seems much smaller for higher HONO concentrations. Moreover, since ambient HONO concentration are mostly less than 10 ppb, information on the stability under such conditions would be even more valuable.

Answer: As explained in the manuscript, the precision of the data shown in Figure 8 will result from the precision of the chemiluminescence instrument and the HONO source and therefore is specified as an upper limit. Since the relative error of the chemiluminescence instrument certainly decreases with increasing mixing ratios, indeed the HONO data at higher levels show an even better precision, e.g. of only 0.4 % for the 4 mg/l data in Figure 3. Since we did not systematically study the contribution of the NO_x-monitor to the precision errors of the measurement data, we simply quantified the upper limit error of both, the source and the NO_x-monitor from the experiment shown in Figure 8. However, since the variability of the HONO source should not depend on the HONO level (see answer to point 5.), we are quite confident that the given upper limit precision error is representative for all experimental conditions. Unfortunately, for the present study we made no long-time experiment at lower HONO levels, for which however the precision error would get higher caused by the lower precision of the NO_x monitor at lower HONO levels.

7. I fully agree with the authors' statement on the advantage of the reported HONO source over the traditional calibration method for instrument based on wet chemical techniques. Since the authors have LOPAP instrument in their lab, it would be helpful if the authors can provide comparison of ambient measurement results calibrated by gaseous HONO and liquid NO_2^- standards.

Answer: Here, the referee misunderstood our conclusion. First the source is ideal for calibration of HONO instruments, for which no simple calibration is possible, e.g. mass spectrometers. Second, for wet chemical techniques the source can be in addition used to characterise instruments, which are under development, e.g. to quantify their sampling efficiencies. However, after an instrument is well characterized, e.g. like the LOPAP instrument, the best calibration available should be used. For the LOPAP technique the accuracy error, when the instrument is classically calibrated by the liquid nitrite standard, can be optimized down to ±3-4 %, which is still lower, than the accuracy error of the HONO source (<10 %, ideally, ca. 6 %, see section 4.2.). For example, when we compared our LOPAP instrument for pure HONO/NO_x mixtures in the EUPHORE smog chamber in two separate campaigns, deviations of <3 % were observed (see Figure 1 in Kleffmann et al., 2006). This high accuracy can not be obtained by calibration with the HONO source. Thus, we will not regularly calibrate our LOPAP instrument by the HONO

source, but by the classical liquid calibration. However, this conclusion may be different for other wet-chemical instruments.