

We thank the reviewer for her/his time and comments, which are reproduced in *black italic font* below. Our responses are shown in regular font. Revised text (as it appears in the manuscript) is shown in blue font. Line numbers are those of the revised manuscript with changes accepted.

*Anonymous Referee #1 Received and published: 5 June 2020*

*This paper discusses the optimization of a HONO calibration source suitable for field work. For many instruments, the source needs to be relatively free of compounds that could interfere with the measurements of HONO. Current methods of HONO production often produce concentrations that vary with operating conditions (humidity, temperature, flow rates), as well as requiring long periods before stable outputs are achieved. Because of issues of stability and reproducibility, the output of HONO calibration methods need to be confirmed in the field with a secondary HONO instrument, often an absolute measurement technique such as absorbance spectroscopy or a chemiluminescent NO<sub>x</sub> analyzer. Ideally, a field calibration source would provide stable and reproducible concentrations of HONO that could be quantified in the laboratory and reliably reproduced in the field, such that a secondary instrument would not be needed for source quantification.*

*The source described in this paper is based on the design of Febo et al. (1995), which has been used extensively by other groups as outlined in the manuscript. The authors describe changes in the design of the source that appear to minimize impurities such as ClNO and NO<sub>x</sub>, and characterize the output of the source using FTIR and TDCRDS instruments. They find that their “optimized source” can produce concentrations of HONO with approximately 97% purity and is stable after 1.5 hours. The authors report HONO concentrations from the source ranging between 1.5 and 3 ppm from FTIR experiments and 11 and 50 ppb from TD-CRDS experiments (with some dilution occurring). The paper does provide some new information regarding the production of a stable, high purity HONO source for instrument calibrations and is likely of interest to the atmospheric chemistry community. While worthy of eventual publication, the paper does not provide sufficient information to give the reader confidence in reproducing the measurements. More experimental details regarding the individual flow rates, humidity, and temperatures should be provided. It is also not clear whether the source routinely produces concentrations of HONO with the stated purity over a range of operating conditions. The authors should include measurements of the HONO concentrations and impurities produced by the source over a range of temperatures and humidities that may be encountered when the source is used in the field. The authors should also provide information on the reproducibility of the source using the same operating conditions after it has been turn off. Illustrating that the output of the source is stable and reproducible from day-to-day might suggest that the source could be robust enough to be used for instrument calibrations without requiring a secondary instrument for quantification in the field.*

Response: We appreciate the reviewer's point of view and agree that the manuscript would be strengthened by including a summary of our results with the optimized source in both the lab and the field.

We added the following on line 152 (to the materials and methods section):

#### "2.4 Field deployment

The HONO source was utilized during the "Study of nitrogen oxides in winter downwind from oil and gas sands" (SNOWDOGS) field campaign in Fort McKay, Alberta, Canada, in January 2020. Its output was quantified in parallel by TD-CRDS and a Thermo 42i-Y NO-NO<sub>y</sub> CL instrument equipped

with a Mo converter heated to 325 °C. This converter and the TD-CRDS quartz inlets were mounted on the roof of a trailer which housed the instruments and the HONO source. The TD-CRDS sampled at a flow rate of ~1.2 slpm per channel through ~5 cm short, 300 µm i.d. stainless steel flow restrictors placed inline after the heated quartz sections and before the Teflon filter assembly. The HONO source output was delivered via a 5 m long, 1/4" (0.64 cm) o.d. and 3/16" (0.48 cm) i.d. FEP Teflon tube to both instruments."

We expanded the text on line 232:

### "3.3 Source stability

The source output gradually decreased over a time scale of weeks of continuous use, which was rationalized by the visible depletion of the HCl permeation tube. However, the source output remained stable and reproducible on shorter time scales. An example FTIR time series is shown in Figure 5, which was acquired after 1 month of intermittent use. After a 1.5 hours stabilization period, the source produced a stable output of 1.57 ppmv of HONO (from >1.0 ppmv of HCl) with a precision of ±35 ppbv.

### 3.4 Source purity and day-to-day reproducibility

The optimized source routinely delivered HONO in high purity (range 96.0% - 98.7%), as long as scrubbed, moisture-containing room air was used as diluent gas (Table 2). When dry cylinder gas was used instead, the source output was stable but contained a larger amount of undesired side products; for example, on July 25, 2019, the output contained 4.6% NO<sub>2</sub> and 8.8% NO + ClNO (Table 2). When used in the field, the performance was similar: with scrubbed air, the HONO purity was 98.5%, whereas with dry cylinder gas, the purity was merely 81.3% (Table 2 and Figure S5)."

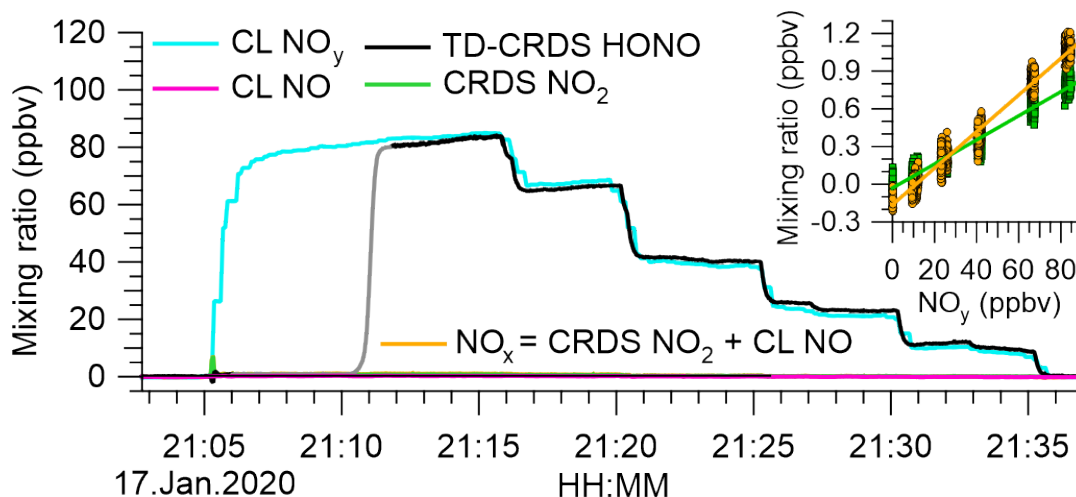
We added Table 2, which summaries our analysis results, on line 414:

"**Table 2.** Summary of TD-CRDS analyses of the HONO source output. The RH of the diluent gas was in the range of 15% to 35%, except for experiments conducted with cylinder gases which are shown below the dashed line. The range of mixing ratios stated is for output after dilution. The stated errors are from regression analyses of plots of NO<sub>2</sub>, NO<sub>x</sub> or NO<sub>x</sub>+ClNO vs. NO<sub>y</sub> and are at the 1σ level. n/d = not determined.

Date	Setting	Diluent gas	Range (ppbv)	HONO (%)	NO <sub>2</sub> (%)	NO <sub>x</sub> (%)	NO <sub>x</sub> +ClNO (%)
Jan 16, 2019	Lab	Scrubbed air	0 - 140	*97.2±0.1	n/d	2.80±0.07	n/d
May 3, 2019	Lab	Scrubbed air	0 - 7	96.0±0.2	1.9±0.2	4.0±0.2	(4.0±0.2)**
May 6, 2019	Lab	Scrubbed air	0 - 93	96.4±0.4	1.9±0.4	3.6±0.4	(3.6±0.4)**
May 10, 2019	Lab	Scrubbed air	0 - 21	*97.6±0.1	1.10±0.03	2.40±0.05	n/d
May 17, 2019	Lab	Scrubbed air	0 - 38	98.7±0.1	0.01±0.02	0.92±0.01	1.25±0.01
May 22, 2019	Lab	Scrubbed air	0 - 14	97.7±0.1	1.29±0.06	1.54±0.06	2.28±0.04
Jan 17, 2020	Field	Scrubbed air	0 - 80	98.5±0.1	1.00±0.05	1.50±0.08	(1.50±0.08)**
Mar 19, 2020	Lab	Scrubbed air	0 - 320	*98.72±0.01	n/d	1.28±0.01	n/d
Jul 25, 2019	Lab	Cylinder O <sub>2</sub>	0 - 95	86.60±0.02	4.60±0.03	n/d	13.4±0.02
Jan 30, 2020	Field	Cylinder N <sub>2</sub>	0 - 50	81.3±0.1	5.90±0.09	n/d	18.7±0.1

\* Upper limit. \*\* The TD-CRDS quartz inlet temperature was ramped between 300 °C and 600 °C; the TD-CRDS mixing ratios at an inlet temperature of 300 °C matched the NO<sub>x</sub> mixing ratios observed with the room temperature inlet, indicating the absence of ClNO."

To the SI, we added



"**Figure S5.** Sample field analysis of the HONO source output. The TD-CRDS and CL instruments sampled scrubbed "zero" air before 21:05 and after 21:36. The HONO source output was added at 21:05:30. Only the CL NO<sub>y</sub> responded because the TD-CRDS quartz inlet temperature was 200 °C. At 21:10, the temperature of the quartz inlet was increased from 200 °C to 600 °C to quantify HONO. The absence of an inflection point and prior agreement with the NO<sub>x</sub> measurement implies the absence of ClNO. At 21:16 and every ~5 min thereafter, the HONO output concentration was decreased by slightly opening the bypass valve. The insert shows scatter plots of NO<sub>2</sub> and NO<sub>x</sub> (calculated by adding CL NO and CRDS NO<sub>2</sub> data) against NO<sub>y</sub>. Slopes and offsets were (0.96±0.05)% and -(30±3) pptv for NO<sub>2</sub> (points shown in green) and (1.46±0.08)% and -(164±4) pptv for NO<sub>x</sub> (data points shown in orange), respectively."

Finally, we revised the statement given in the abstract on line 15:

"The source produces gas streams containing HONO in air in > ~~95%~~ **97%** purity relative to other nitrogen oxides." to account for the observation of (96±0.2)% purity on May 3, 2019 (Table 2).

*Specific comments:*

*Methods:* As mentioned in the paper, previous studies have demonstrated that the production of HONO by reaction R4 requires the gas stream to be humidified. However, the authors do not state the humidity of the gas stream used in their experiments.

Response: We added the following on line 88: "For the experiments shown in this manuscript, the relative humidity of the diluent gas stream was in the range of 15% to 35%."

*Page 4, line 88: Is there any reason for the 20 ccm dilution with O2?*

Response: The additional flow is probably not essential, but we found it practical to keep part of the setup under flow of a clean gas - our laboratory air contains surprisingly high levels of NO<sub>x</sub> delivered from the building's air intake, plus the continued flow would remove any impurities that might build up. The use of a second mass flow controller was also advantageous as it allowed the residence time and HCl concentration to be changed on the fly without disturbing the permeation tube setup (which can take quite a long time to return to a stable output when flows are changed).

We modified the text on line 90 as follows:

"The permeation tube was placed inside a glass chamber (VICI Dynacalibrator Model 120) whose temperature was controlled at 25.0 °C and which was continuously flushed at a flow rate of ~0.15 L min<sup>-1</sup> with room air scrubbed using activated charcoal for a period of several days [into a fume hood](#). The use of scrubbed air ensured that the gas stream contained water to maintain efficient HONO production (Schiller et al., 2001).

The HCl output was diluted in a gas stream of O<sub>2</sub> (~20 mL min<sup>-1</sup>); [this gas stream also served to continuously flush the connecting tubing when not in use.](#)"

*If so, why O2 and not N2, zero air, or scrubbed room air?*

Response: The reviewer is correct that either N<sub>2</sub>, zero air or scrubber air could have been used. We chose O<sub>2</sub> because an O<sub>2</sub> cylinder was already in place for the O<sub>3</sub> generator. No changes were made.

*Page 4, last paragraph: How much dilution was typical? What are final flow rates? More experimental details should be provided.*

Response: We diluted the output by factors between 5 and 200, depending on how much HONO we desired to deliver on any particular day at a flow rate marginally larger than the TD-CRDS inlet sample flow. We modified the paragraph as follows:

"To deliver HONO in atmospheric concentrations (i.e., < 10 ppbv), a portion of the source output was directed towards waste with the aid of a pump and a needle valve. The output concentration could be rapidly changed ([typically by factors between 5 to 200](#)) by adjusting the position of the needle valve. The remaining output was diluted using scrubbed air and directed towards the instruments [at a final flow rate slightly larger than the sampling requirement of the instruments.](#)"

*Fig. 1: The position of the needle valve and dilution do not match the written description. The figure only shows the input of the TD-CRDS being diluted and not the FTIR, while the text describes dilution before both instruments.*

Response: As stated on line 107, the needle valve was used to deliver HONO in atmospheric concentrations (i.e., < 10 ppbv). The FTIR sampled the output without dilution, and the Figure is accurate as shown. We clarified this on line 111:

"Gas streams exiting the HONO sources (prior to dilution) were analysed using an FTIR spectrometer"

*The schematic would benefit with typical flow rates.*

Response: This information has been added to Figure 1.

*Page 7, line 161: In this discussion, the authors are probably referring to reaction R5, and not R6.*

Response: We thank the reviewer for catching this error. It has been corrected (line 177). We also corrected another error of this type on line 165.

*Page 7, line 169: It appears that the improvement in source 2 is only a reduction of ClNO contamination, as both the NO and NO<sub>2</sub> concentrations increased. This should be clarified.*

Response: The reviewer's observation is correct. The issue with both source 1 and source 2 was that there was too much HONO produced, which can generate side products by either R-1 or R5. In source 2, more HONO was produced than in source 1 (because the rate of R5 was reduced) which increased the rate of NO and NO<sub>2</sub> produced via R-1.

We added the following on line 185: "... an improvement over source 1 in terms of unwanted ClNO production but still inadequate."

*Page 8, equation 2: Check the equation – there appears to be an error translating the fonts.*

Response: Apologies - this was an error converting word (.docx) to pdf format. Equation (2) is

$$[\text{Observed}]_{\text{total}} = [\text{NO}_x] + [\text{ClNO}] \left( 1 - e^{-A_{\text{ClNO}} \times e^{-\frac{E_{\text{A,ClNO}}}{RT}} \times t_{\text{res}}} \right) + [\text{HONO}] \left( 1 - e^{-A_{\text{HONO}} \times e^{-\frac{E_{\text{A,HONO}}}{RT}} \times t_{\text{res}}} \right)$$

This has been corrected in the revised document.

*Fig. 5: The authors should define the lighter shaded points in both plots. Are the lighter shades indicating points while the source is stabilizing? If so, why are there lighter shade points at the end of the time series?*

Response: Our apologies - the two lighter shade points at the end of the time series should have been in dark shade as well; this has been corrected. We also modified the caption as requested.

**Figure 5.** Time series of HONO and HCl mixing ratios derived from FTIR analysis of the undiluted HONO source output. The NaNO<sub>2</sub> was placed in line at 10:10. Data acquired during the initial period are shown in light grey colour. The shaded areas represent the average  $\pm 2\sigma$  after the source output had stabilized (after 11:45; data points shown in black colour). The  $1\sigma$  precision of the HONO data was  $\pm 35$  ppbv and that of the HCl data was  $\pm 42$  ppbv. The HCl mixing ratios are an underestimate because the widths of their absorption lines are less than the FTIR's resolution of  $0.5 \text{ cm}^{-1}$ .

*The authors should clarify how they determined that the output had stabilized.*

Response: In the caption of Figure 5, we had stated "The shaded areas represent the average  $\pm 2\sigma$  after the source output had stabilized (after 11:45; data points shown in black colour)."

Since we didn't apply a mathematically rigorous criterion to determine output stability, we changed the above to:

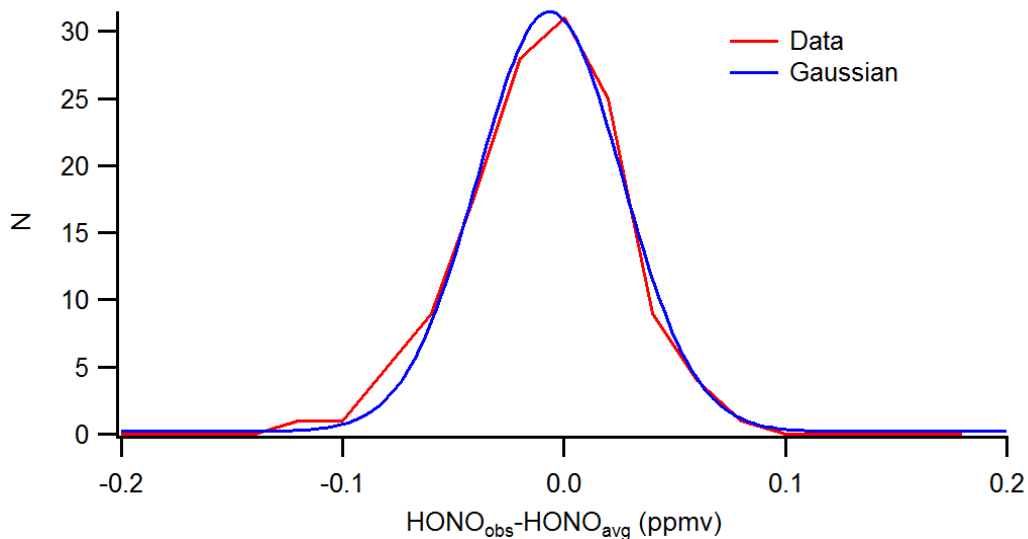
"The shaded areas represent the average  $\pm 2\sigma$  after the source output had ~~had~~ was judged to have stabilized (after 11:45; data points shown in black colour)."

We had judged whether the output was stable (or not) by visual inspection but also had performed a few simple statistical tests for corroboration.

A stable output is achieved when the output mixing ratio is not changing. For the data shown in black, this criterion is met since the slope of a linear regression fit is  $-(0.4 \pm 1.9) \times 10^{-6} \text{ s}^{-1} \approx 0$ .

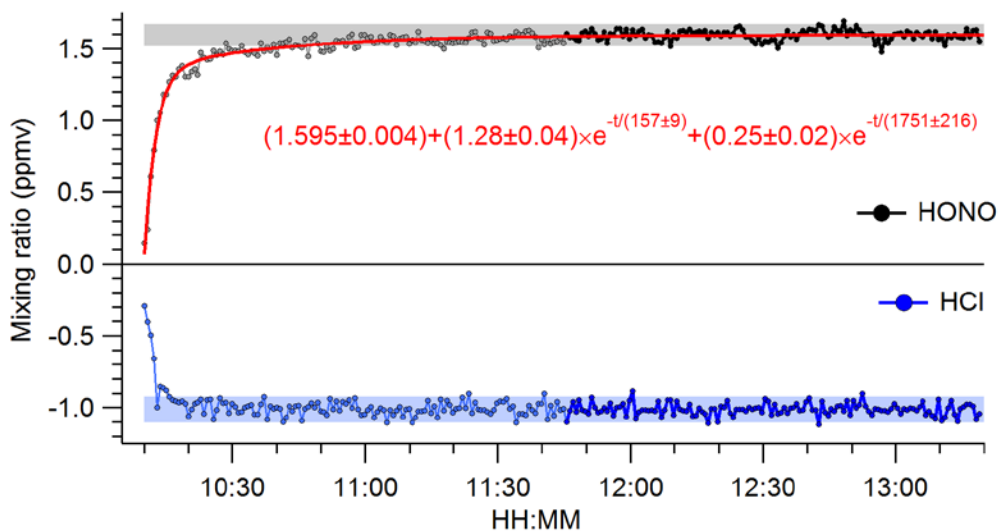
We also calculated the average ( $\mu$ ) and standard deviation ( $\sigma$ ) for this period which were 1.596 and  $\pm 0.036$  ppmv. The residuals during this time period were normally distributed (i.e., reproduced by a Gaussian equation, see figure below).

The  $\mu \pm 2\sigma$  interval is shown as a grey area in Figure 5; since the noise is normally distributed, this interval is expected to encompass 95% of the data; for the data shown in black, 6 of the 132 (~4.5%) are outside this confidence interval.



The above confirms that the output during the chosen period was stable (i.e., confirms that "the source output had stabilized" as we had stated in the caption of Figure 5), but it does not justify the choice of the left limit to what is called a stable period in Figure 5 (which we had estimated at 11:45:30).

Expanding on the above discussion, we applied a double exponential fit to the HONO data in Figure 5:



The first time constant of this fit was  $(157 \pm 9)$  s, corresponding to the mixing time of gas in the FTIR multipass cell (assuming plug flow  $450 \text{ cm}^3$  at a flow rate of  $170 \text{ cm}^3 \text{ min}^{-1} \sim 160$  s). The second time constant was  $29.3 \pm 3.6$  min. The fit is within 1% of the limiting mean at 11:46:56 in Figure 5, which is very close to the "eye-ball" estimate.