

## ***Interactive comment on “A portable, robust, stable and tunable calibration source for gas-phase nitrous acid (HONO)” by Melodie Lao et al.***

**Anonymous Referee #1**

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In the manuscript by Lao et al. the development and characterisation of a portable calibration source of HONO is described. The generation of HONO is based on a former source developed by Febo et al. (1995) and which is based on a reaction of gaseous humidified HCl with solid sodium nitrite. In contrast to the former study HCl is produced by a modified custom-built permeation source and the sodium nitrite is simply deposited on a PFA reaction tube. Although the source produces lower HONO levels than demonstrated in the former study by Febo et al., I have several concerns with the manuscript.

Major Concerns:

1) Calibration source:

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While I realize that the source can produce more or less constant HONO levels under certain conditions (see below) this is not a calibration source. If you want to use this source e.g. to calibrate a new HONO instrument, you need another instrument to characterize the source before under fixed experimental conditions. Even the HCl-concentration cannot be used to calculate the expected HONO level because of the parallel “H<sub>2</sub>O reaction”, see below. Thus a HONO source is described here but not a calibration source! A calibration source could be e.g. the HONO source by Taira and Kanda (1990) using known Henry’s law coefficients of HONO in the acidic bubble solutions and measured gas and liquid flows (NaNO<sub>2</sub>/H<sub>2</sub>SO<sub>4</sub>).

2) Stability of the source:

Already in the title the stability of the HONO source is high-lighted. However, when looking into detail to the study, I cannot see this stability, which is much lower than in the original study by Febo et al., but also lower than in several other studies.

Already the HCl production of the permeation source is not very stable and the variations are not well described, cf. e.g. Fig. 4a and Fig. S7. Also when you compare the HCl emission of the different PDs listed in Tab. 1, 2, 3 variations are observed which are much larger than the specified singles errors. E.g. In Tab. 1 the source PD-6a emits at 40 °C 0.21±0.01 ppb HCl, whereas in Tab. 2 and Tab 3 0.08±0.002 ppb and 0.33±0.007 ppb are listed? What are the reasons for this variability?

Also the stability of the HONO source is very low. E.g., it takes more than 24 hours until the source produces stable HONO, see Run 1 in Fig. 3. Or why is the HONO source so unstable over 90 hours in Fig. 4b? These spikes are not really well explained and do not completely disappear even after long running time (see Fig. S10, Run 2). And even when the source is running for long time a variability of the HONO emission of 24 % is specified (see Figure 5b and line 525). This means that even when the HONO source is calibrated with very high accuracy by an independent method before (e.g. by precise NO<sub>y</sub>-measurement using chemiluminescence and a carbonate denuder)

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than the uncertainty of a field calibration using the source is only  $\pm 25\%$ . This is not sufficient for many applications, when e.g. daytime levels of HONO are compared with calculated PSS levels under urban conditions, when the PSS is only a factor of two lower than measured values (in this case the uncertainty of the “unknown daytime source” would be  $\pm 50\%$ !).

The original source by Febo was much more stable and could also in theory be tuned to lower HONO concentrations by using more dilute HCl solutions (not tested in Febo et al., but works. . .). Also the simple source by Taira and Kanda is much more stable and shows precisions of a few percent. This source was further modified by using a temperature controlled stripping coil and also shows much higher stability (see [https://quma-shop.de/images/LOPAP%2003%20HONO%20Source%20short\\_v2.pdf](https://quma-shop.de/images/LOPAP%2003%20HONO%20Source%20short_v2.pdf)). I used this source during the FIONA intercomparison (<http://euphore.es/fiona/fiona.html>), which is a 19” instrument producing stable low HONO levels (ca. 1 % precision in the low ppb range) in a few tens of minutes which can be quickly and exactly tuned in a few minutes simply by changing the nitrite solution.

3) Purity of the source: In the present study a purity of  $>90\%$  is mentioned and impurities of NO of 5.5%/6 % are specified (lines 656 and 658). Typically NO impurities are formed by the bimolecular decomposition of HONO on surfaces producing equal amounts of NO and NO<sub>2</sub> (R3). Thus for me at least the NO<sub>x</sub> impurities are higher than 10 %, which is much higher than in the original paper by Febo et al. where NO<sub>x</sub> impurities of  $<0.5\%$  were determined at  $<20$  ppm. Also the loss of HCl is not negligible. There is a clear small Cl<sup>-</sup> signal in Figure 2 with the source on (I expect this is of the order of few percent of the HONO level, please expand the Cl<sup>-</sup> signal). In contrast the simpler source by Taira and Kanda will not show HCl emission, since non-volatile H<sub>2</sub>SO<sub>4</sub> can be used.

4) Formation mechanisms: In the present study two formation mechanisms are identified, the “HCl-“ and the “H<sub>2</sub>O-mechanism”. While the acid displacement mechanism of HONO by the strong acid HCl is clear (see Febo et al.) the H<sub>2</sub>O-mechanism should

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be better characterised (see line 406: “. . .beyond the scope of this work.”) since this is the main reason for the low stability of the HONO source for the initial phase when the source is started (e.g. first 24 hours for Run 1 in Figure 3, or  $\gg 40$  hours in Figure 6, the final steady state level will be 5 ppb in Fig. 6, see HCl emission of PD-6c in Table 1). The authors propose that NaOH is formed when H<sub>2</sub>O reacts with the sodium nitrite (see line 405). However, I expect that they still have CO<sub>2</sub> from their zero air generator which decrease the pH in the adsorbed water surface layers on the NaNO<sub>2</sub> to pH = 5.5 at which the fraction of HONO to nitrite is ca. 0.5 % (see pK<sub>a</sub> of HONO) making small HONO emissions possible in the absence of HCl. With extended operation of the source the increasing amount of NaHCO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> formed on the surface will decrease the pH leading to lower HONO formation. This mechanism could also explain the much higher HONO emissions of the annular denuder compared to the PFA-tubes when using the same HCl permeation source (see the 6.2 ppb in Table 2 compared to the 24.5 ppb, see line 626, or the 400  $\rightarrow$  25 ppb in Fig. 6, when using PD-6c). Only when this non-stable side reaction can be minimized there is a chance for a really stable and predictable (by [HCl]<sub>g</sub>) HONO source!

Specific Concerns:

The following concerns are listed in the order how they appear in the manuscript.

Line 22: while 90% purity is possible, I do not see the 99% (see above)!

Lines 42-43: HONO levels of up to 18 ppb have been determined in the Po-valley (Milan) in Los Angeles and in Santiago de Chile.

Line 46: Start with 2010a when using references by Veres et al. for the first time (and 2010b in line 113).

Line 66: The study by Villena et al., 2011 is not on HONO?

Line 80: A modified HONO source of the one by Taira and Kanda is missing (Kleffmann et al., J. Phys. Chem. A, 2004, 108, 5793-5799, see also link above).

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Line 85: The advantage of the source by Taira and Kanda is that non-volatile dilute H<sub>2</sub>SO<sub>4</sub> can be used bearing no risk of HCl emissions for incomplete acid displacement.

Line 104: The reason why the nitrite was stirred in Febo et al. is a) to minimize concentration peaks of HONO in channels in the nitrite powder to reduce the quadratic reaction kinetics of R3 and b) to increase the assessable surface area for complete acid displacement.

Line 109-110: The stabilization of the original HONO source by Febo et al. takes much shorter than the present source (see Febo et al., 1995). When I used that source several years ago it took only ca. 1 hour to get stable HONO levels, e.g. when the temperature of the HCl bath was changed. And other sources are even faster (see major concerns).

Section 2.1 and 3.1: The coating procedure of the PFA tubes is not clear for me. In section 2.1 it seems that all the nitrite added by the 3 ml coating solution stay inside the tube until the solvents are completely evaporated. However in Section 3.1 only a small fraction of the nitrite is recovered. Where is the rest? Or is the solution decanted similar to the procedure used for the annular denuder (see line 158)?

Figure 1 and S3: Are each two holes (1/2") in the aluminium block (see S3) used for one HONO source (1x HCl and 1x NaNO<sub>2</sub>, see Figure 1), i.e. can two parallel HONO source lines be used here?

Section 2.3 and S2: The set-up of the HCl permeation source is not clear for me. Is the 1/4" tube filled with liquid HCl inserted into a 1/2" PFA tube which is temperature controlled in the Al-block and flushed by the zero air? Is the smaller tube fixed in the middle of the larger PFA tube (how?) or is it simply lying on the ground of the larger tube? Please show a more detailed figure of the HCl permeation source.

Line 209 and Fig.1: Why is the low HONO source flow rate of only 100 sccm used and later diluted to 1.1 slm? If the source should be tuned to high HONO levels (ppms, see

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line 664), the HONO concentration in these 100 sccm are 11 times higher leading to stronger decomposition of HONO by R3. Why not using 1.1 slm for the reaction?

Line 214: Typically also 1 % glycerol is added to a coating solution of a denuder (see coating of the NaNO<sub>2</sub> reaction devices, see line139)?

Section 3.2: caused by the non stable reaction by "H<sub>2</sub>O" (or CO<sub>2</sub>?) this side reaction should be minimized, see major concern. I cannot follow the statement in lines 335-337 – HONO production by this reaction is not defined and not constant, see Figure 6!

Lines 350-353. For me the source is already unstable at 40 °C, see peaks at 2 PM in Figure S7.

Table 1 and section S2: The production of the HCl tubes seems to be really "tricky" since similar tubes produce variable HCl emission by one order of magnitude! In addition the given errors of 0.01 ppb for the first three HCl concentrations are only a short term precision but not for longer time, compare data in Tables 2+3.

Line 380-384: Why are the HCl emissions decreasing by one order of magnitude for a time period of 2 years? Is this in accordance with the expected decrease of the liquid HCl concentration (e.g. 6 M) from the loss of gaseous HCl? In addition, a 30 % decrease is not similar to an order of magnitude (2 -> 0.21...).

Table 2: ADEs of only >55% and >84 % can be determined based on the given errors of HONO (e.g. 0.14/0.31...) and not >99%.

Figure 2: The red shaded area is almost invisible during zero. In addition I do not see any blue shaded area?

Line 458-459: That is not true for Run1 in Figure 3 (>24 h...)

Figure 3, 5, S9, S10, S12: Why do the authors not use a more precise HONO instrument or higher HONO levels? The precision of 0.4 ppb of the NO<sub>y</sub> monitor is too low to determine any dependencies at HONO levels of ca. 2 ppb. Typically the concentrations

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should be more than 10 times higher than the precision of the instrument used. . .

Line 477 and Figure 4: I do not understand the low stability of the HCl/HONO production (variability by factors, see Figure 4b. . .)? From where are these peaks coming even after 15 days of use, see Figure S10?

Line 501: should be “after” and not “before” or “Figure 4b-c”? In Fig 5 the output is more or less stable (+-25%...).

Line 505-506: I cannot follow that statement, see major concerns.

Line 563-565: Both data shown in Figure S10 are not stable (+- factor of 2) and I cannot follow the RSD of only 16.5%? Cf. the red data at 5, 10 and 37 h.

Line 592: The relative stability of the HONO source is lower at 40 °C compared to 50°C see Table 3 ( $1 \pm 0.5 = +50\%$  and  $2 \pm 0.5 = +25\%$ ). So I do not understand that statement?

Line 606-607 and Table 4: I do not understand the lower output of the quartz tubing? Normally quartz is hydrophilic and can be much better wetted by aqueous solutions than the very hydrophobic PFA, leading to higher expected nitrite levels for the quartz?

Lines 624-630: The reason for the unstable and much higher HONO emissions ( $\gg$ [HCl]) is the higher surface area and the unwanted side reaction by “H<sub>2</sub>O” (or CO<sub>2</sub>?), see above. . .

Line 643-644: The source by Febo et al. was much more pure ( $>99.5\%$ ) than the present one (see 6 % NO = 12 % NO<sub>x</sub>, see R3 => purity 88%...).

Line 662-664: While the former study showed impurities in the 10 % range at 4 ppm, this source shows similar impurities already below 1 ppb (see line 657), which is very untypical with respect to the quadratic reaction kinetics of reaction R3. And again in Febo et al. the purity was higher than 90% even in the ppm range.

Line 675: Should be  $<25\%$  see line 560?

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Line 858: Processes

Line 887 and 902: . . .Res. Atmos.

Line 988: 10155-10171

Line 993: 9093-9106

Line 999: delete the second Vecera, Z.

Line 1010: D23302

Line 1061: L15820

Line 1074: 1681

Supplement Section S1, second paragraph, line 5: should be 47 and 51 sccm, see Figure 1?

Section S1, last paragraph before Figure S1: The temperature should be electronically limited to 150 °C (see harmful degradation products for PFA in the case of a malfunction. . .).

Figure S3: Why are larger hole diameters (0.6”) used in the Al block for the 0.5” PFA permeation source tubes? There would be better heat transfer, if the holes would be only slightly larger than the PFA tubes (e.g. 0.51”) getting them into direct contact with the aluminium.

Figure S7. From where do the peaks during the temperature ramps (40-50°C and 50-60°C) result? There should be constant increases of HCl similar to the ramp between 30-40 °C?

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