Interactive comment on "HONO Measurement by Differential Photolysis" *by* C. Reed et al.

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Received and published: 26 April 2016

We, the authors, would like to thank the reviewer for their comment and time taken in reviewing our submission. Please find our responses, point-by-point below.

"This approach may not necessarily require an accurate NO2 measurement in order to measure HONO (although that would greatly simplify the analysis, and seems to be assumed). This approach does require that any interferences in the NO2 measurement at 385 nm are unchanged when HONO is measured at 395 nm. This assumption is implicit, but should be stated explicitly, and defended at some level in the text."

The technique does require accurately knowing the NO2 conversion efficiency, and thus knowing NO2. The technique does not require knowing NO however at all.

We consider photolytic interference being different at different wavelengths e.g. BrONO2 and calculate the uncertainty to be minimal considering the abundance of

BrONO2. We have expanded the section on measurement artifact, interferences and uncertainties accordingly, being specific about their sources and significance.

"A paper in review at ACPD by these authors shows that undesired thermal decomposition of PAN presents an interference in their NO2 measurement (http://www.atmos-chem-phys-discuss.net/acp-2015-789/). Further, possible interferences from thermal decomposition of methyl pernitrate (CH3O2NO2) (Browne et al., ACP, 11, 4209–4219, doi:10.5194/acp-11-4209-2011, 2011) may also compromise the NO2 measurement in certain regions. Are these an issue for the HONO measurement by difference from NO2 in this approach, and if not, why not?"

Under the reasonable assumption that the sample gas illuminated at 385 and 395nm experiences the same temperature, then thermal interferences only affect the NO2 measurement as at both wavelengths the interference would be equal. Differences in NO2 conversion efficiency introduce some uncertainty in the artifact arising from thermal decomposition of NOy. We would hope that anyone wishing to measure NO2 or HONO using photolytic converters would as a prerequisite eliminated these sources of error as a matter of course.

We have added discussion of the uncertainties arising from artifacts.

"Further, no discussion is given of the spurious NO2 "artifact" signal that can be generated when illuminating NO2-free air at UV wavelengths (e.g., Kley and McFarland, J. Atmos. Technol., 1980). This NO2 "artifact" signal can be large and variable, and if different at the different wavelengths used to infer HONO in this technique, can represent a major bias in inferred HONO unless accounted for. Are there similar "artifact" signals for HONO when HONO-free air is irradiated at 395 nm? The authors should discuss these issues, quantify them in their instrument, and include them in a comprehensive uncertainty analysis before this paper is acceptable for publication."

All data was corrected for NO, NO2 and HONO 'artifact' signals by sampling an overflow of zero air generated from compressed air or BOC BTCA-178 zero air both of

which were subsequently passed through 13x molecular sieve, sofnofil, and activated carbon filters as was oxygen for ozone generation. Artifacts were for NO = 0ppt, NO2=319ppt, HONO=49ppt (319+49), NOy=500ppt. For the CAPS NO2 instrument there is no artifact as zero is referenced to zero air.

In the case of NO when measuring ambient air on campaign the NO artifact was taken as the night time NO value (in answer to another point below).

We have added a discussion of measurement artifacts, their uncertainty and correction for.

"P4, line 7: change to read "...gives a sample residence time of 0.96 seconds assuming plug flow..."How good is the plug flow assumption?"

Gas enters the converter, which is perfectly cylindrical, in an annular ring at one end and exits by annular ring at the other. Response time to 95% of maximum is 1 second or better- indicative of plug flow.

We have added that response to 95% maximum is within 1 second.

"P5, lines 9-10: "It is noted that at both 385 nm and 395 nm there is potential interference from BrONO2 (or in fact any other compounds which photolyse to give NO at either wavelength)..."A point that first comes up here: the potential interferences also include spurious NO chemiluminescence when the photolysis cell is illuminated at either wavelength in the absence of gas-phase nitrogen compounds. This has been termed an "artifact" signal in NO2 photolysis and is thought to arise from undesired photolysis of nitrogen compounds (likely nitric acid or ammonium nitrate, but others are possible) adsorbed on the photolysis cell walls. At times this artifact signal has been substantial (e.g. on the photolytic NO2 measurement flown on the NASA ER-2 aircraft described in Del Negro et al., JGR, 1999) and should not be neglected. I did not find any discussion of the NO2 "artifact", or the possibility of its being different at the different wavelengths used to infer HONO abundance. The "artifact" needs to be

quantified fully and its uncertainties discussed as a possible source of error in HONO inferred by this technique."

We have added a discussion of the artifact correction as noted above in response to a previous comment.

"P8, lines 2-5: "This 2 apparent HONO conversion determines the limit of detection, which is the ability of the analyser to discriminate the difference in signal arising from photolysis at the two different wavelengths from photon counting noise." Because this method is a difference of three numbers (NO, NO2, and HONO) that can vary independently, the effective limit of detection should also depend on the NO concentration, the NO-to-NO2 ratio, and the NO-to-HONO ratios. For example, when ambient NO is very low (e.g. after dark in remote regions) the 'background' signal (really, ambient NO plus the fraction of NO2 photolysed at 385 nm) from which HONO is determined will be relatively low, and the effective HONO LOD will improve due to better precision in the 'background' signal according to photon counting statistics. Conversely, when ambient NO is very high (e.g. in urban areas at the surface, close to traffic sources) the 'background' signal can be very high, thus the effective HONO LOD must be degraded. Please include a more rigorous treatment of the HONO limit of detection."

Agreed, at the request of reviewer #1 also we have given more thorough treatment to the determination of LOD. We have also made better distinction between LOD, uncertainty and precision which was previously unclear.

"P8, lines 9-11: "The effect of the back reaction of OH + NO, reforming HONO, before detection of NO, thus reducing the NO signal in the NOx/HONO measurement in the presence of HONO was calculated using a box model..."The ensuing discussion uses a reaction time of 0.11 seconds, which assumes this reaction begins only after the sample exits the photolysis cell. Is it really that simple? There is a similar back-reaction that involves NO + O3P, reforming NO2, which if not accounted for will bias the NO2 measured at 385 nm and thus HONO inferred by this technique. Further, what about

HONO and/or NO2 that are photolysed immediately upon entering the photolysis cell? The reaction time to reform either HONO or NO2 can take place in the photolysis cell as well. Both back-reactions, including those occurring in the photolysis cell residence time of about 1 second, should be modeled."

The effect of the back reactions within the photolytic converter is what is modelled and shown in figure 5 and its associated discussion. The effect of NO + (O3p) and NO + OH back-reactions are what are calibrated for during NO2 and HONO calibration. The back reaction after exiting the converter (in the absence of UV) was discussed to demonstrate that it does not affect overall sensitivity and is not a source of bias as the [OH] is necessarily different at each wavelength.

We have also made it clear that the input model of the OH back reaction was initiated with the output of a model of the 1s residence time within the photolytic converter while illuminated.

We have clarified the discussion of figure 5 to indicate more precisely what is modeled, whilst also being more specific about what is being calibrated for when we determine the converter efficiency in section 2.4.

"P12, line 23: "...NO offset was taken between these times." What does this mean? Please rephrase for clarity."

That is the NO artifact correction made by assuming it is equivalent to a stable nighttime NO value in remote regions (Lee et al., 2009), away from any source, where NO should be zero in the presence of eg > 15ppb O3.

"P13, lines 1-2: "There is reasonable agreement between the established LOPAP method of HONO measurement 1 and that provided by the pHONO instrument without correction or calibration." This is a value judgement and should be changed to express a quantitive measure of agreement."

We have added the R-squared ($\sim$0.6) value of the correlation between the two mea-

surements.

"P13, lines 3-4: "During 2 the high ozone and high HONO events observed on the 1st and 2nd especially there is very good 3 agreement between the two." Yes, but what about the data observed on June 30 shown in Figure 6? The measurements diverge by a factor $\sim$2 and lines 21-22 suggest the June 30 data were not plotted in Figure 7. I find the focus on days characterized as "high HONO" to be troubling. The comparison at low values is equally useful and should be included. Please include all the available data in Figures 6 and 7, and explain why a subset was chosen for the linear fit in Figure 7. Is the linear fit single-sided or does it allow for uncertainties in both X and Y values, as it should? Please confirm that a bivariate fit weighted by instrument precisions was used. If at times the two measurements disagree systematically by a factor of two, what does this imply for the accuracy and selectivity of either measurement? It would help to also show the time series of NO and NO2 data in Figure 6, because it is likely the pHONO measurement will be at its best at relatively low NOx and high HONO values."

All data in figure 6 is shown again in figure 7 including the 30th of June. Apologies for the confusion caused by our phrasing which we have now corrected. We were suggesting that there was better agreement on 1st and 2nd , rather than the data only being form the 1st and 2nd. A bivariate fit was used covering all data.

We focused on high HONO days as they fell at the beginning of the campaign when there is certainty that the instrument was operating well. However, as requested by reviewer #1 we will make available the raw unprocessed data, full time series, and NOx data as supplemental information.

High HONO values necessarily occur at times of high NOx so the reviewers' theory that the pHONO measurement would be best at high HONO and low NOx cannot be tested. We have changed figures 6 and 7 to include all the time series of both instruments operating together. which spans 30th June to 6th July. The pHONO instrument operated until 25 July until being damaged by water ingress.

We believe that periods of great disagreement are due to very local contamination – corresponding to periods of high nighttime NO in the case of the 3th June. It is possible that the FAGE exhaust, which is a vat of sofnofil sorbent to scrub the % levels of NO emitted. It is likely that some HONO is evolved by this sorbent and that due to its position both instruments would not necessarily sample the plume.

"P14, lines 11-13: "During 11 field tests the photolytic HONO instrument agreed reaǏ-sonably well with the established LOPAP 12 instrument,.." This is a value judgement and should be changed to express a quantitive measure of agreement."

In line with a previous comment this has been changed to indicate the R-squared value as a measure of agreement.

"Fig. 1. For clarity please use colored text to identify the different spectra. The caption describes the colors, but is cut off after line 2 in my PDF version."

The caption is correct in the online version.

"Fig. 2. The error bars should show the standard error of the mean – please confirm in the caption."

The error bars are the standard deviation of the mean. We have amended the figure caption of this figure (and Fig 4) to clarify this.