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Atmospheric Measurement Techniques Discussions

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

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We would like to thank the reviewer for their comments and suggestions, and for taking the time to review our submission. Please not that supplementary information has been uploaded in addition to this response.

"The instrument’s HONO measurements are compared to measurements using an FT-IR system at high concentrations. The “absorptivity data” (i.e., IR line strengths or absorption cross sections) were based on an “internal FT-IR cross-section database”, as provided by a personal communication. Since these FT-IR data have not been published in the peer-reviewed literature and the methods used to determine the IR line strengths are not described, these nice comparison experiments are just as much a validation of the FT-IR as they are a validation of the present technique.... In other words, the favorable comparison observed is not a *strong* validation of the differential photolysis method. Note that Lee et al. (2012) found large errors (more than a factor

of two) in a similar unpublished IR database."

Indeed, it is a validation of the Wuppertal cross-section database as much as it is of our instrument. The reviewers reference (Lee et al., 2012) describes different wavenumbers and a different technique (QCL) to that described here (FT-IR).

We have therefore taken the published line strengths found by (Barney et al., (2000) who also found discrepancies between different published values. This has changed our figure only slightly and not affected the point we were showing i.e. that the correlation is linear up to a point, before deviating. The revised FT-IR values using data from (Barney et al., (2000) are $\sim$ 7% lower, still lie within our measurement uncertainty of $\sim$12% with respect to the 1:1 correlation.

We have also noted that there are several published cross-sections, none of which agree particularly.

"The determination of the LOD and precision needs to be more fully described. The text states that the apparent HONO conversion efficiency determines the LOD, and states that the LOD is 40 ppt min-1. As described in equation 1, [HONO] is proportional to the difference between NO2+385 and NO2+395, divided by the difference in HONO conversion efficiencies. The precision is thus determined by the quadrature sum of the two channel’s readings. What is the absolute precision (i.e., in ppt NO) of the NOx analyzer’s 30 second readings at typical NO + NO2 + HONO concentrations? This would appear to determine the theoretical detection limit. In actual field use, variability of the ambient NO, NO2, and HONO concentrations could limit this precision significantly, as described on pg. 13. What were typical LOD’s for the field data? It would be VERY illuminating to include a short time series, at least in the SI, that shows the actual raw NO, NOx+385 and NOx+395 measurements along with the derived HONO concentration – for both the chamber data (calm) and ambient data (occasionally turbulent)."

The theoretical limit of detection is always determined by the photon counting noise, taken as the 2 sigma standard deviation of the 1hz pre-chamber zero measurement averaged over some time by $1\sqrt{n}$ where n is the number of points which is divided by the sensitivity in counts per second, per ppt, that is in the case of NO, for NO2 and HONO this value must be divided by their respective conversion efficiencies also. The linear response of NO chemiluminescence analysers means that the precision should remain the same at any mixing ratio. In practice the zero noise increases in more polluted (and therefore greater NOx) environments. The LOD, for all intents and purposes, doesn't change for NO, NO2, HONO, however, the uncertainty and precision in HONO is greatly affected by atmospheric variability in NO, NO2, HONO which using a switching channel to determine NO2 and HONO. This proof-of-concept deign demonstrates that all too well, however this is not unique to this instrument, any switched channel instrument i.e. most commercial single channel NOx analyzers suffer this problem. Weybourne proved to be much more turbulent than expected, whilst conditions ultimately led to damage to the instrument.

We excluded data which exceeded 5% variability over 1 minute (Two 30 second cycles). This means that the effective limit of detection ranged from $\sim$ 5ppt to 100 ppt averaged over a minute assuming a differential conversion efficiency of 90%.

We have made available as supplementary information the time series of raw (unprocessed and not interpolated) NO,NO2,HONO measured in the HIRAC chamber over a range of dilutions as a figure, as well as the full time series of ambient data taken at Weybourne as a CSV file.

We have also given more thorough treatment to the determination of LOD and been careful to keep the distinction between LOD, uncertainty, and precision more clear.

"Also, though it is common to state an LOD as xyz “ppt min-1”, I recommend more accurately stating it as “xyz ppt with one-minute averaging”, since 40 ppt/min does not mean 80 ppt in 2 minutes, etc."

Agreed, we have changed all instances to xyz ppt averaged over 1 minute

"The description of how many analyzers are used is conÂňfusing. Pg 3 line 9 states that “a dual channel” instrument (singular) is used, but pg. 12 states that “two NO chemiluminescence analyzers operate in parallel with duplicated independent equipment.” (plural). Based on this and the rest of 2.1, I initially inferred that there are two dual-channel analyzers, and in each of them NO is continuously measured in one channel and the other channel alternates between “NO + 385 phoÂňtolysis products” and “NO + 395 photolysis products. Or is there just one dual channel instrument – one channel measures NO and the other alternates between the 385 and 395 nm converters? The answer (the latter) was not apparent until pg. 13 where the field data is described."

We have amended the description to make it clear that there is only 1 analyser which has 2 channels (NO and NO2/NOx/HONO). We had described it as “essentially” two analysers operating in parallel, which caused confusion.

"Pg 2, line 3, remove “...thought to be...”. In addition to the two references provided on vehicular HONO emissions, the authors may wish to include references for more recent HONO emission studies, for example Lee at al 2011 (aircraft and diesel), Rappengluck et al 2013 (on-road vehicles), and Roberts et al 2010 (biomass burning)."

Agreed, we have added these references at the reviewers suggestion.

"Pg 2 lines 17 and 24 – note that QC-TILDAS and the “dual laser – quantum cascade laser” are the same instrument. Probably best to just describe as QC-TILDAS."

Thank you to the reviewer for pointing out this duplication which has been removed

"Pg 7 line 4: This sentence was confusing: “NO2 was measured directly by CAPS using an EPA certified Teledyne AP T500U, to avoid any HONO interference”. It would be good to clarify that CAPS is the technique (from Aerodyne) and that the physical instrument is sold by Teledyne. Otherwise it is confusing to those who are familiar with the CAPS instruments sold directly by Aerodyne. On this note, the authors should actually address potential interference of HONO in the CAPS NO2 measurement since it is based on absorption of light in a bandpass of 440 – 460 nm. Glyoxal is a known interference with the CAPS NO2 measurement.... What about HONO at the calibration concentrations used?"

The Teledyne instrument is described by the manufacturer as a CAPS NO2 instrument. We were using CAPS as a generic term, but have now made it clear that Aerodyne developed this patented technology. We have added discussion of the possibility of interference in CAPS instruments – from aerosol nitrate (mitigated by a HEPA filter in this instrument). Glyoxal, which absorbs between 400-460 nm, but is absent from the zero air during the calibration of our instrument. HONO absorbs <390nm (Teledyne CAPS operates with a 450nm bandpass) thus HONO is not an interference in this measurement, nor is HNO3, some of which is produced by our HONO source.

"Pg 8 line 4 – should this be "...apparent differential conversion of 6.54%", instead of "...apparent conversion of 6.54%"?"

We have changed added the word "differential" at the reviewers suggestion.

"Figure 6 and 7 and accompanying text: This is an encouraging first set of measureÂň-ments and comparison for the pHONO instrument, and well described. Any comÂň-ments on the occasional time periods when the pHONO measures significantly higher than the LOPAP? For example, roughly between 03:00 and 06:00 on 30/6/2015, when pHONO's numbers are 2 to 3x higher?"

Indeed the two methods at times disagree greatly, more than the inherent uncertainty of the switching design in turbulent conditions. We believe this is due to a very local strong source, namely the exhaust of the FAGE instrument. The FAGE vents a high flow of percent level NO through what is essentially a vat of sofnofil sorbent, which we believe oxidizes NO to HONO to some extent, so whilst the NO and NO2 is removed, the HONO is not. There were also other possible sources of local HONO e.g. a tractor nearby.

We have added text as to sources of disagreement.

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Please also note the supplement to this comment:
http://www.atmos-meas-tech-discuss.net/amt-2016-17/amt-2016-17-AC1-supplement.zip

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