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Atmospheric Measurement Techniques Discussions

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

Anonymous Referee #1

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This manuscript describes a clever method of quantifying atmospheric HONO using a chemiluminescence NO analyzer equipped with two photolytic converters with different wavelengths. The material is certainly relevant to the scope of AMT and the methods appear sound and in general well described. I recommend it for publication in AMT after the issues below are addressed.

Major comments: 1. 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*

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Discussion paper

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 (2012) found large errors (more than a factor of two) in a similar unpublished IR database.

2. 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).

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.

Medium importance comment: The description of how many analyzers are used is confusing. 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 photolysis 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.

Minor comments: 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).

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.

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?

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

Figure 6 and 7 and accompanying text: This is an encouraging first set of measurements and comparison for the pHONO instrument, and well described. Any comments 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?

References Lee, B. H.; et al., "Effective line strengths of trans-nitrous acid near 1275 cm-1and cis-nitrous acid at 1660 cm-1 using cw-QC TILDAS". Journal of Quantitative Spectroscopy & Radiative Transfer 113 (15), 1905-1912 (2012)

Lee, B. H.; et al., "Measurements of Nitrous Acid in Commercial Aircraft Exhaust at the Alternative Aviation Fuel Experiment". Environmental Science & Technology 45 (18), 7648-7654 (2011)

Rappenglück B., et al., (2013) "Radical Precursors and Related Species from Traffic as Observed and Modeled at an Urban Highway Junction", J. Air Waste Manage. Assoc., 63:11, 1270-1286, DOI:10.1080/10962247.2013.822438

Roberts et al., "Measurement of HONO, HNCO, and other inorganic acids by negative-ion proton-transfer chemical-ionization mass spectrometry (NI-PT-CIMS): application to biomass burning emissions", Atmos. Meas. Tech., 3, 981–990, 2010 www.atmos-meas-tech.net/3/981/2010

1. Does the paper address relevant scientific questions within the scope of AMT? YES 2. Does the paper present novel concepts, ideas, tools, or data? YES 3. Are substantial conclusions reached? YES 4. Are the scientific methods and assumptions valid and clearly outli ned? YES with exceptions as noted in my review 5. Are the results sufficient to support the interpretations and conclusions? YES 6. Is the description of experiments and calculations sufficiently complete and precise to allow their reproduction by fellow scientists (traceability of results)? YES 7. Do the authors give proper credit to related work and clearly indicate their own new/original contribution? YES 8. Does the title clearly reflect the contents of the paper? YES 9. Does the abstract provide a concise and complete summary? YES 10. Is the overall presentation well structured and clear? YES 11. Is the language fluent and precise? YES 12. Are mathematical formulae, symbols, abbreviations, and units correctly defined and used? YES 13. Should any parts of the paper (text, formulae, figures, tables) be clarified, reduced, combined, or eliminated? NO 14. Are the number and quality of references appropriate? YES with exception noted in review 15. Is the amount and quality of supplementary material appropriate? NO –exemplary raw data of NO and both NOx* channels should be included

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