

Response to Reviewer 2:

The following discussion includes the reproduced text from the reviewer (bold), along with our detailed responses and the corresponding changes (italics; eliminated text is struck through) made to the revised manuscript. All page and line numbers refer to the original manuscript.

J.Collett (Referee 2)

Stockwell et al. report a thorough and satisfying performance evaluation of a catalyst based approach to measuring particulate reactive N. Although others have explored similar approaches, the work has largely gone unpublished or lacked the thorough evaluation provided by the current authors. There is a compelling need to quantify total reactive N in airborne particles and I commend the authors for their efforts. I also commend them for the thoroughness of their evaluation and the care in which they describe limitations to their approach (e.g., the need to look at particulate OC in a CO₂-free stream, the importance of eliminating PILS-ESI-MS matrix/ion suppression effects by using single component standards, etc...). Their findings will be very useful to the broader atmospheric chemistry community, extending from those interested in source characterization to those interested in deposition and particle effects on human health and radiative scattering. I have a few suggestions for minor changes to improve the manuscript.

We thank Dr. Jeffrey Collett for his positive review and useful comments, which have added value to this paper. Additional specific responses are included below.

1. Title: I found the title confusing and somewhat misleading. The focus is primarily on N and primarily on direct measurement of particulate (or total) reactive N. The title should better reflect that.

We agree that it is important to straightforwardly describe the focus of this paper in the title. While we are characterizing a catalyst approach to quantitatively convert particulate nitrogen and organic carbon, we also believe it is important to present comparisons to other mass measurement systems as this may be of interest to scientists interested in alternate calibration approaches for their particle mass measurement systems. Thus, we have changed the title to better describe the manuscript

Existing title: "Characterization of a catalyst-based total nitrogen and carbon conversion technique to calibrate particle mass measurement instrumentation"

New title: "*Characterization of a catalyst-based conversion technique to measure total particulate nitrogen and organic carbon and comparison to a particle mass measurement instrument* "

2. Abstract: The mention of particulate organic carbon conversion in the abstract is, I suppose, appropriately brief. I do suggest that the authors here refer to "efficient" or "complete" conversion rather than simply conversion. I also suggest they point out here the important challenges of determining particulate OC by this method against a high concentration ambient background, as described in the manuscript itself.

We have added "efficient" before "conversion" and briefly describe this method's shortcomings for application to ambient sampling of particulate carbon.

P1 L24 We added text: "*efficient*" before "conversion"

P1 L25 We added new text to the abstract: "*However, the application of this method to the atmosphere presents a challenge due to the small signal above background at high ambient levels of common gas-phase carbon compounds (e.g. CO₂).*"

3. Section 3.1.1. The authors refer here to experimental methods not described in the methods section of the manuscript. I suggest an Experimental Details section be added on methods for checking gas-phase conversion efficiency. This would allow the authors to clearly convey information about calibration standards and comparison gas phase measurement methods. Section 3.1.1, for example, talks about apparent errors in the assumed ammonia absorption cross-section, but this is confusing because the reader has not been told how this is relevant to the gas-phase ammonia measurement method. The latter has not been specified.

We have added a section to more clearly describe the gas-phase conversion experiments. Per Reviewer 1's suggestions we have reorganized the manuscript, thus this new section was added to the "Experimental design" section prior to our discussion focusing on methods for determining particle phase conversion efficiency.

New added text/section:

"2.2.1 Methods for determining gas-phase conversion efficiency"

"The efficiency of conversion of several N-containing gases by the N_r catalyst was determined through addition of a number of representative compounds that were calibrated independently. The NO signal from the converted species was then compared to the signal from an NO in N_2 standard (5.38 ppmv, Scott-Marrin Inc., Riverside, CA) that was used as the working standard for this project. Typical calibration levels were in the range of 50 to 100 ppbv as determined by the mass flow controllers used to mix the standard into the measurement stream. The standards used for each compound and their associated calibrations were as follows.

The NO_2 standard stream was produced from the NO working standard through gas-phase titration with a small stream of O_2 in which O_3 had been produced by photolysis at 184.9 nm using a mercury discharge lamp. This technique is used routinely for NO_x and NO_y measurement systems (Williams et al., 1998) and allows straightforward determination of NO_2 conversion provided care is taken not to over-titrate the NO stream to produce NO_3 and therefore N_2O_5 . The uncertainty in the NO_2 conversion determination is simply the propagated errors in the subtraction of the signals before and after titration.

The ammonia (NH_3) conversion was examined using two different NH_3 sources, a gas mixture (3.1 ppmv in N_2 , Scott-Marrin) and a permeation device (Kin-Tek, LaMarque, Texas). Care was taken with these standards to keep them under flow for periods of several days in order to insure any system surfaces were equilibrated. The calibration of these standards was accomplished by ultraviolet (UV) absorption spectroscopy at 184.9 nm wavelength using an instrument described by Neuman et al, (2003), and based on absorption cross-sections reported in the literature (Tannenbaum et al., 1953; Lovejoy, 1999; Froyd, 2002). The uncertainty of NH_3 conversion was propagated based on the uncertainties in flow rate and UV absorption determinations.

The hydrogen cyanide (HCN) standard consisted of a commercial gravimetric mixture of HCN in N_2 (10 ppmv, GASCO Oldsmar, FL), which was mixed into the system using a mass flow controller. The specified uncertainty of this mixture was $\pm 10\%$, and the standard concentration was verified using long-path Fourier-transform infrared (FTIR) spectroscopy to within the stated uncertainty. The HCN standard was used to produce a gas phase stream of cyanogen chlorine (ClCN) by reaction with chloramine-T, a non-volatile chlorinating agent, which has been described previously (Valentour et al., 1974). To do this, a small stream (5 standard $cm^3\ min^{-1}$) of the HCN standard was combined with humidified Zero Air (ZA, 60% RH, 30 standard $cm^3\ min^{-1}$) over a bed packed with glass beads coated with a solution of chloramine-T. The glass beads were prepared by coating glass 3 mm outer diameter (OD) beads

with a 2 g 100 mL⁻¹ solution and packing ~20 cm³ of them in a 12.7 mm OD PFA tube and flowing ZA over them until dry. The reaction was shown to be essentially 100% ($\pm 10\%$) by proton-transfer reaction mass spectrometry (PTR-MS) when conducted in a humidified atmosphere ($RH \geq 60\%$), by FTIR analysis of the HCN and ClCN in the gas stream before and after chlorination.

The isocyanic acid (HNCO) standard was prepared according to the methods described by Roberts et al. (2010), in which the trimer, cyanuric acid, was thermally decomposed at 250°C in a diffusion cell to produce a steady stream of HNCO, which was then calibrated by long-path FTIR spectroscopy. Initially, this source has the potential to produce NH₃ as an impurity, most likely because of the presence of trace amounts of water. Keeping the source under flow and above 120°C at all times when not in use was found to reduce the NH₃ impurity to negligible levels (<5%), as measured by PTR-MS. The uncertainties in the HNCO standard were propagated from the uncertainties in the HNCO cross section (Northwest-Infrared, PNNL), the NH₃ subtraction, and flow rates. Standard streams of both nitrobenzene and trimethylamine were produced using gravimetrically prepared solutions and a commercial liquid calibration device (Ionicon, Innsbruck, Austria). The uncertainties in these liquid calibration standards were estimated from the propagated uncertainties in the solution concentrations and the liquid and gas flow rates

The conversion of nitrous oxide (N₂O) is a potential interference in the N_r method as N₂O is not typically considered a reactive nitrogen compound in the troposphere. Several experiments were conducted to determine the extent of this potential interference using a 10.1 ppmv N₂O standard. The resulting conversion efficiency ranged from 0.03% to 0.05% in dry and humidified air respectively. These can be considered upper limits for this interference as we cannot be completely sure that there were no N_r contaminants (e.g. NO₂) in the N₂O standard.”

We added the following references to accompany the above text:

P19 L3 Added text: “Froyd, K. D.: Ion induced nucleation in the atmosphere: Studies of ammonia, sulfuric acid, and water cluster ions, Ph.D., Department of Chemistry, University of Colorado, Boulder, Colorado, 282 pp., 2002.”

P21 L29 Added text: “Lovejoy, E. R.: Ion trap studies of H⁺(H₂SO₄)_m(H₂O)_n reactions with water, ammonia, and a variety of organic compounds, *Int. J. Mass Spectrom.*, 190/191, 231-241, 1999.”

P25 L1 Added text: “Tannenbaum, E., Coffin, E. M., and Harrison, A. J.: The far ultraviolet absorption spectra of simple alkyl amines, *J. Chem. Phys.*, 21, 311, doi: <https://doi.org/10.1063/1.1698878>, 1953.”

P8 L6-7 Existing text: “We verified the efficiency of conversion of a range of gas phase N_r compounds in this catalyst system using calibrated gas mixtures or standard streams and auxiliary analysis methods.” New text: “We verified the efficiency of conversion of a range of gas phase N_r compounds in this catalyst system using calibrated gas mixtures or standard streams and auxiliary analysis methods as described in Sect. 2.2.1.”

P8 L7-9 We eliminated the text: “We compared the total N_r signal measured as NO, where NO was calibrated using NO standards in nitrogen (Scott-Marrin Inc., Riverside, CA) to the known amount specified by the calibration method.”

P8 L11-12 Existing text: “The uncertainties in the measured conversion efficiencies encompass the propagated errors in each calibration method.” New text: “*The uncertainties in the measured conversion efficiencies are the propagated errors in each calibration method, and in all cases the range encompasses 100 % conversion*”

4. p. 8, line 29: It seems a bit odd here that the authors refer just to negligible interference from N₂O conversion in biomass burning sources. Why only discuss BB and not other (e.g., auto exhaust, ag, etc...) sources. The focus makes a bit more sense given later discussion about the Missoula FIREX experiment, but since this manuscript is really addressing a more broadly applicable approach, it would be helpful to broaden the N₂O interference discussion beyond BB

We have added the following text to extend the N₂O discussion to other sources so that biomass burning is not implied as the only important source mentioned in the manuscript:

P8 L30 New text added: “*N₂O emissions from other sources (e.g. natural and anthropogenic agricultural sources, fossil fuel combustion, or animal waste) can be significant, therefore the interference from N₂O conversion must be considered*”

5. top of p. 9: It is my sense that it is not so uncommon for NO concentrations to be in the range of 10s of pptv in remote regions. I suggest the authors better justify or moderate their claim that an NO interference of 28 pptv is “clearly a negligible amount in almost any atmospheric context.”

The Reviewer raises a valid point here, which we address below.

P9 L1-2 Existing text: “an upper limit that is clearly a negligible amount in almost any atmospheric context” New text: “*an upper limit that is generally a negligible amount in almost any atmospheric context except in more remote regions.*”

6. Section 3.1.4 and Fig. 6. This is an interesting timeline of deriving “excess” reactive N from the new instrument measuring a smoke plume. Do the authors have a measurement of HNO₃ in the airstream? I suggest that modified combustion efficiency (MCE) be added as a parameter in Fig. 6, if available, to help make the authors’ point re: periods of smoldering vs. flaming combustion.

HNO₃ was not measured during the experiment though we’d expect very low concentrations from biomass burning as much of the HNO₃ formed likely reacts quickly with NH₃ to form particle nitrate (Yokelson et al., 2009; see reference below). The Reviewer brings up a useful suggestion to add MCE to the figure to better support the differences in emissions between smoldering and flaming, therefore we have added MCE to panel (c) of Fig. 6 and the following additions to the text:

See: Yokelson, R. J., Crounse, J. D., DeCarlo, P. F., Karl, T., Urbanski, S., Atlas, E., Campos, T., Shinozuka, Y., Kapustin, V., Clarke, A. D., Weinheimer, A., Knapp, D. J., Montzka, D. D., Holloway, J., Weibring, P., Flocke, F., Zheng, W., Toohey, D., Wennberg, P. O., Wiedinmyer, C., Mauldin, L., Fried, A., Richter, D., Walega, J., Jimenez, J. L., Adachi, K., Buseck, P. R., Hall, S. R., and Shetter, R.: Emissions from biomass burning in the Yucatan, Atmos. Chem. Phys., 9, 5785-5812, <https://doi.org/10.5194/acp-9-5785-2009>, 2009.

P11 L15 Added text: “*The modified combustion efficiency (MCE) is a measure to estimate the relative contribution of flaming and smoldering combustion that occurred over the course of a fire, where the MCE is defined as the ratio of $\Delta\text{CO}_2 / (\Delta\text{CO}_2 + \Delta\text{CO})$ (Yokelson et al., 1996). A higher MCE value (approaching 0.99) designates relatively pure*

flaming combustion (more complete oxidation) and a lower MCE (~ 0.75 – 0.84) designates more smoldering combustion.”

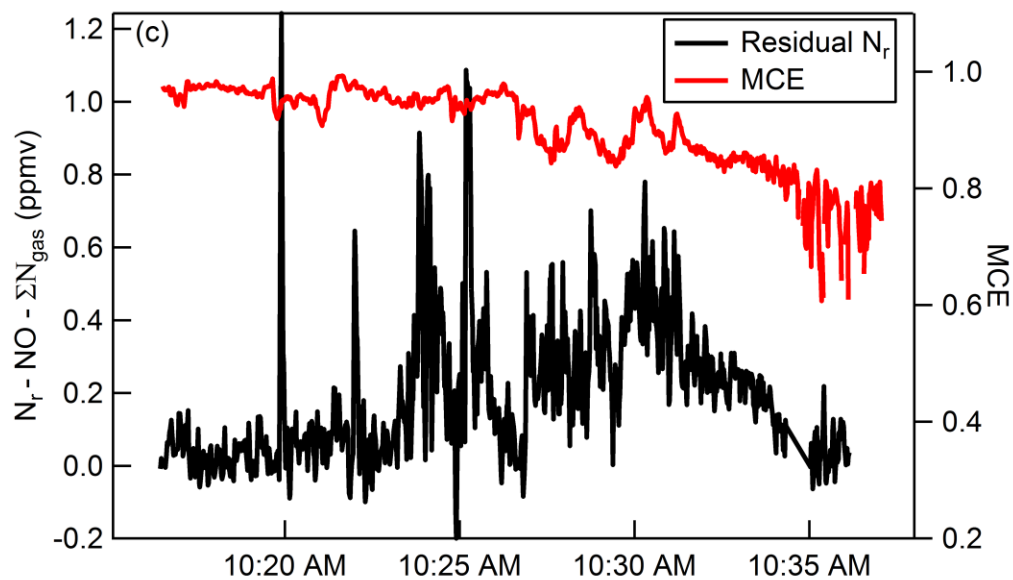
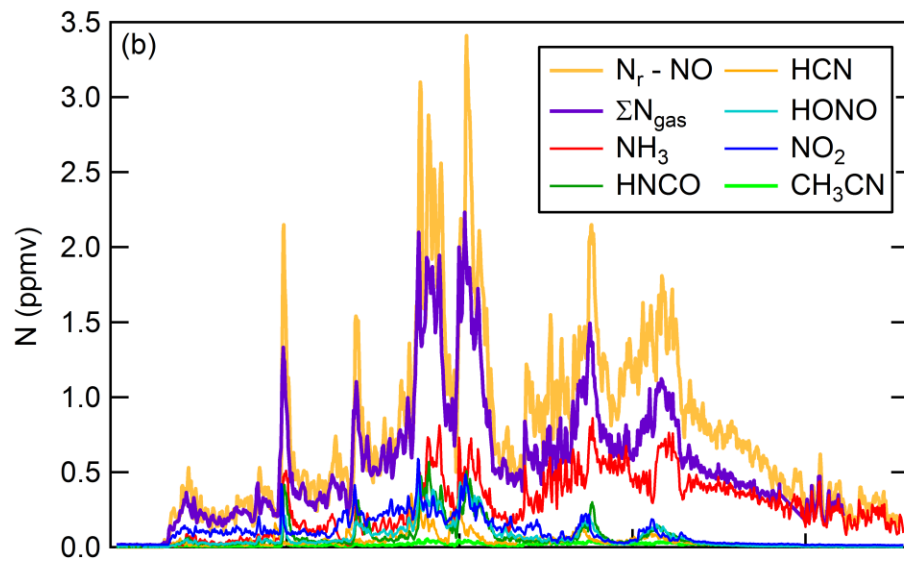
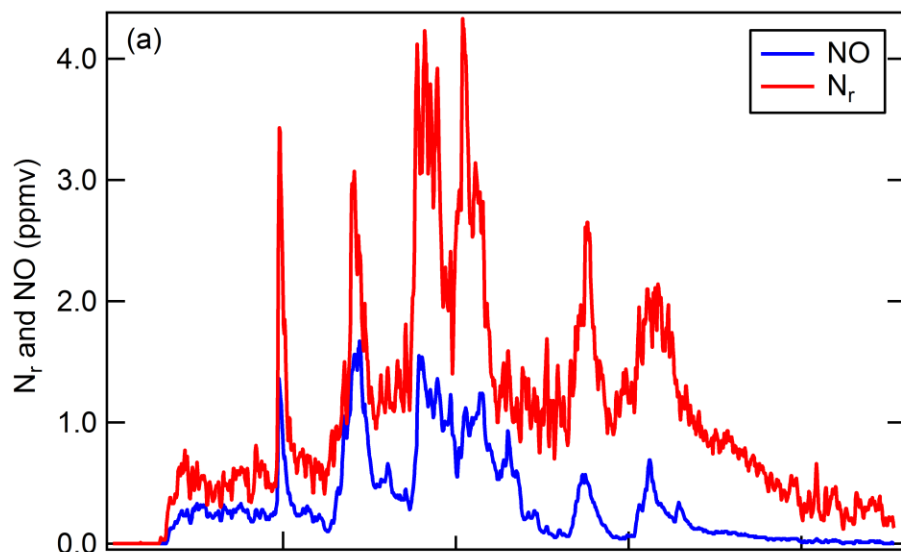
P11 L16-17 Existing text: “it is likely that particulate ammonium contributes to the excess N_r signal measured during periods dominated by smoldering combustion” New text: “*it is possible that the residual signals are due to particulate N-containing compounds. Particulate ammonium may contribute to the excess N_r signal measured during periods dominated by smoldering combustion ($MCE < 0.90$).*”

P11 L17-18 Existing text: “, while particulate nitrate likely accounts for some N_r signal during the flaming dominated stages as shown in Fig. 6.” New text: “*The oxidized N-containing gas phase species are relatively more abundant during the initial part of the fire, so particulate nitrate could account for some N_r signal during the flaming dominated stages as shown in Fig. 6.*”

P32 Figure 6 caption; Existing text: “(c) Residual N_r in ppmv” New text: “*(c) Residual N_r (black) in ppmv with modified combustion efficiency overlaid (MCE, red).*”

P25 L3 Add reference “*Yokelson, R. J., Griffith, D. W. T., and Ward, D. E.: Open path Fourier transform infrared studies of large-scale laboratory biomass fires, J. Geophys. Res., 101, 21067–21080, doi:10.1029/96jd01800, 1996.*”

Please see updated Figure below:



7. typos: a. p.6, line 11: change "least-squared" to "least-squares" b. p. 6, line 35: change "promoted" to "promote" p. 12, line 20: change "liens" to "lines"

Thank you for bringing these minor mistakes to our attention. We have corrected the mistakes as follows:

P6 L11 Existing text: “least-squared” New text: “least-squares”

P6 L35 Existing text: “promoted” New text: “promote”

P12 L20 Existing text: “liens” New text: “lines”

The following includes voluntary changes to references, which includes several updates

P21 L1-4 Update the Kupc reference to: “Kupc, A., Williamson, C., Wagner, N. L., Richardson, M., and Brock, C. A.: *Modification, calibration, and performance of the Ultra-High Sensitivity Aerosol Spectrometer for particle size distribution and volatility measurements during the Atmospheric Tomography Mission (ATom) airborne campaign, Atmos. Meas. Tech.*, 11, 369-383, <https://doi.org/10.5194/amt-11-369-2018>, 2018.”

P7 L24 Change “Kupc et al. 2017” to *Kupc et al., 2018*”

P7 L31 Change “Kupc et al. 2017” to *Kupc et al., 2018*”

P7 L34 Change “Kupc et al. 2017” to *Kupc et al., 2018*”

P24 L9-11 Update the Selimovic reference to: “Selimovic, V., Yokelson, R. J., Warneke, C., Roberts, J. M., de Gouw, J., Reardon, J., and Griffith, D. W. T.: *Aerosol optical properties and trace gas emissions by PAX and OP-FTIR for laboratory-simulated western US wildfires during FIREX*, *Atmos. Chem. Phys.*, 18, 2929-2948, <https://doi.org/10.5194/acp-18-2929-2018>, 2018.”

P11 L10 Change “Selimovic et al., 2017” to “*Selimovic et al., 2018*”

P20 L23-27 Update the Koss reference to: “Koss, A. R., Sekimoto, K., Gilman, J. B., Selimovic, V., Coggon, M. M., Zarzana, K. J., Yuan, B., Lerner, B. M., Brown, S. S., Jimenez, J. L., Krechmer, J., Roberts, J. M., Warneke, C., Yokelson, R. J., and de Gouw, J.: *Non-methane organic gas emissions from biomass burning: identification, quantification, and emission factors from PTR-ToF during the FIREX 2016 laboratory experiment*, *Atmos. Chem. Phys.*, 18, 3299-3319, <https://doi.org/10.5194/acp-18-3299-2018>, 2018.”

P11 L10 Change “Koss et al., 2017” to “*Koss et al., 2018*”