

Response to Reviewers:

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.

We thank both Referees for their thorough comments and constructive suggestions, which were helpful in improving the manuscript. We have addressed their issues and concerns to the best of our ability.

Anonymous Referee #1

**In this well written manuscript, the authors present the characterization of a catalyst based total nitrogen and carbon conversion technique to calibrate particle mass measurement instrumentation, as clearly reflected in the title of the manuscript. Set-up, methodology, and conversion efficiencies for particle-bound nitrogen species are thoroughly discussed. The authors convincingly describe, that the instrument is capable of quantitatively converting a range of particle-bound nitrogen species and provides an online signal of total reactive nitrogen from both gas- and particle-phase, which is very useful for the assessment of nitrogen cycling in the atmosphere. The conversion of particle-bound carbon via a platinum catalyst is described for a number of organic compounds in laboratory-generated aerosols, while an application to the atmosphere remains challenging due to the small signal compared to background CO<sub>2</sub>. Nevertheless, a simultaneous detection of total reactive nitrogen and total carbon in one instrumental set-up is a promising perspective. However, the organization of the manuscripts' content could be improved to increase the value of the paper. For example, clearly dividing the subjects instrument characterization (instrument set-up and experiment design, gas-phase N<sub>r</sub> conversion efficiency, particle-phase N<sub>r</sub> conversion efficiency, particle-phase C conversion efficiency, proof of concept - N<sub>r</sub> measurements of biomass burning), and particle mass measurement calibration (laboratory generated aerosols, comparison with PILS-ESI/MS) in sections 2 and 3. A reader could then very quickly see why this new instrument is worth learning about. After addressing content organization and the specific comments listed below, the paper will be very well suited for publication in AMT.**

We appreciate the Reviewer's positive comments, and agree that the manuscript could be reorganized to clarify the experimental approach, motivation, and conclusions. We have divided the manuscript into the following sections: (1) Introduction; (2) Experimental details including (a) instrument descriptions with an added total carbon (Cy) section; (b) experimental design, which includes an added section on methods for determining gas phase conversion efficiency per Reviewer 2's suggestion. The section "particle generation, measurement and characterization" was renamed "methods for determining particle phase conversion efficiency" and a few sentences were added or removed for organizational clarity within this section. (3) Instrument characterization, including both gas and particle conversion efficiency discussions and our "proof of concept" biomass burning emissions measurements; The section discussing the N<sub>r</sub>-particle conversion efficiency was divided into two subsections (a) Challenges using the DMA/SMPS to determine N<sub>r</sub>-particle conversion efficiency and (b) Determining N<sub>r</sub>-particle conversion efficiency using a DMA and UHSAS. (4) Application to calibrate the PILS-ESI/MS using comparisons with the PiLS-ESI/MS (5) Summary and Conclusions. Sentences throughout the manuscript were occasionally shifted to a new section (see for e.g. the new total carbon (Cy) system section in the experimental details section now incorporates sentences originally included in the results section) or to a more appropriate section to improve the organization as suggested by the Reviewer. While these organizational changes added to the value of this paper, the pages, lines, and a few figure numbers were altered

from the original manuscript. As a result the following changes/discussion following the Reviewer's specific comments will continue to refer to the original manuscript.

The following section was added to the Experimental details:

*“Total carbon (C<sub>y</sub>) system*

*Measurements of total carbon (C<sub>y</sub>) were accomplished by catalytic conversion to carbon dioxide (CO<sub>2</sub>) and detection using a CO<sub>2</sub> analyzer. The high-temperature (750°C), platinum catalyst (Fig. 1) in the N<sub>r</sub> system should quantitatively convert carbon containing species to CO<sub>2</sub> in the presence of air. Gas-phase carbon conversion across similar precious metals has been studied extensively (see for example the Pt catalyst used in Veres et al., 2010). The total flow through the Pt catalyst was set to ~1.5 standard L min<sup>-1</sup> and was then split before the MoOx catalyst. In our sampling scheme 0.5 sL min<sup>-1</sup> of flow was directed to a LICOR 6251 (LI-6251; Lincoln, NE) CO<sub>2</sub> analyzer, while the remaining flow, 1 sL min<sup>-1</sup>, was directed through the MoOx catalyst and to the NO-O<sub>3</sub> chemiluminescence detector as detailed in Sect. 2.1.1. Run in this manner, the conversion of compounds that contain both N and C atoms can then be measured simultaneously using the NO-O<sub>3</sub> chemiluminescence detector and LI-6251 detector in parallel.*

*The LICOR instrument was internally referenced to scrubbed zero air. At ambient CO<sub>2</sub> levels, it is challenging to retrieve reliable measurements since the signal relative to the background abundance of CO<sub>2</sub> is small. In order to evaluate organic carbon conversion efficiency, our approach relies on using ultra-pure air for aerosol generation and carrier gas flow, therefore ambient CO and CO<sub>2</sub> is eliminated. The LI-6251 was calibrated with sub-5 ppm CO<sub>2</sub> standards (Scott-Marin Inc., Riverside, CA) in ultra-pure air. Due to the low signals levels and the uncertainty of the low concentration CO<sub>2</sub> standards, the overall uncertainty of the CO<sub>2</sub> measurements below 1 ppmv presented in this work is ± 10% for 10 second averages.”*

**Specific comments:**

**1. Could you think of a more representative name or acronym for your instrument? The term N<sub>r</sub> instrument does not totally reflect the purpose of the instrument in my opinion**

While we appreciate the Reviewer's suggestion to create an alternate acronym this is primarily an instrument for on-line measurement of gas- and particle-phase total reactive nitrogen. We explicitly state in the introduction that the converter coupled with the NO-O<sub>3</sub> chemiluminescence detection is referred to as the “N<sub>r</sub> system.” For the purposes of organic carbon measurements we direct the sample stream following the heated platinum catalyst to an off-board NDIR CO<sub>2</sub> detector and there are additional sampling restrictions since the small signal compared to background CO<sub>2</sub> limits ambient sampling. When we discuss organic carbon conversion specifically, we highlight that the method of conversion is across the platinum catalyst only, which is the front-end of our “N<sub>r</sub> system.” We have also added a subsection to the instrument descriptions section to specifically detail the total carbon measurement approach. Additionally, future experiments will focus on quantifying sulfur conversion followed by SO<sub>2</sub> detection and we wish to hold off on naming the complete nitrogen/carbon/sulfur instrument until it is fully characterized.

**2. Please include more recent references on P. 2 L. 6, e.g., Jimenez, et al. 2009, Science; Hallquist et al. 2010, ACP; etc.**

The Reviewer was right to point out that we have not included more recent publications or reviews, thus we have added the two references suggested to the appropriate paragraph.

P2 L7 Added text: “Jimenez et al., 2009; Hallquist et al., 2010”

P19 L10 Added reference: “Hallquist, M., Wenger, J. C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen, J., Donahue, N. M., George, C., Goldstein, A. H., Hamilton, J. F., Herrmann, H., Hoffmann, T., Iinuma, Y., Jang, M., Jenkin, M. E., Jimenez, J. L., Kiendler-Scharr, A., Maenhaut, W., McFiggans, G., Mentel, Th. F., Monod, A., Prévôt, A. S. H., Seinfeld, J. H., Surratt, J. D., Szmigielski, R., and Wildt, J.: *The formation, properties and impact of secondary organic aerosol: current and emerging issues*, *Atmos. Chem. Phys.*, 9, 5155-5236, <https://doi.org/10.5194/acp-9-5155-2009>, 2009.”

### **3. You sometimes speak of “these experiments” or “these studies” in the manuscript, please consider revising these statements for clarity and readability**

We thank the reviewer for their suggestion and agree that using the phrases “these experiments” and “these studies” are confusing and unnecessary, so we have revised the manuscript in several places by eliminating these phrases as follows:

P4 L11-12 Existing text: “The primary objective of these experiments is to characterize particle conversion” New text: “*The primary objectives are to characterize particle conversion*”

P4 L34 Existing text: “The operation of this instrument during these experiments often required considerable de-tuning to keep the instrument count rates below the roll-over point of the photon counting electronics (approximately 5 MHz), thus the detection limit was closer to 0.1 ppbv for these measurements.” New text: “*The operation of this instrument often required considerable de-tuning to keep the instrument count rates below the roll-over point of the photon counting electronics (approximately 5 MHz) for the particle concentrations generated, thus the detection limit was closer to 0.1 ppbv (corresponding to 0.3  $\mu\text{g m}^{-3}$  for aerosol nitrate).*”

P5 L27 Existing text: “A detailed description of the PILS used in these studies can be found” New text: “*A detailed description of the PILS can be found*”

P12 L33 Existing text: “The inorganic salts selected for this study” New text: “*The inorganic salts selected for the comparison between  $N_r$  and the PILS-ESI/MS instruments*”

P15 L13 Existing text: “The  $N_r$  particles tested in these experiments span the” New text: “*The  $N_r$  particles tested span the*”

### **4. The purpose of the MoOx catalyst, i.e., reducing NO<sub>2</sub> to NO, is not clearly stated in section 2.1**

We have added the following sentence:

P4 L31-32 “*The heated MoOx catalyst reduces the remaining NO<sub>2</sub> to NO.*”

### **5. Please carefully check through the manuscript again and try to revise extensive and anecdotic paragraphs for conciseness. Exemplarily, please have a look at lines 6 – 29 on page 7 and revise this paragraph.**

While we have edited the suggested paragraph, we feel the information that was not eliminated from the paragraph is important and the organizational changes detailed earlier and completed per Reviewer 1's suggestion more clearly supports their inclusion. The specific revised text is indicated below:

P7 L6-29 Existing text: "In these experiments particle diameters from 100 to 600 nm were selected and the multiply-charged particles in the size distribution were accounted for as described below. For the liquid concentrations and atomizer conditions we used, the DMA output size distribution is a multi-peaked population consisting not only of singly charged particles but also particles with multiple (mostly two or three) charges. The multiply charged particles can contribute significantly to the overall mass and must be considered when calculating particle mass. The distributions of singly, doubly, and triply charged particles can vary depending on the solution concentration. We measured atomized size distributions using the scanning mobility particle sizer (SMPS; Wang and Flagan, 1990) function of the DMA (physical diameter,  $D_p = 1\text{-}1000$  nm). The DMA transfer theory (Knutson and Whitby, 1975; Stolzenburg, 1988) with Wiedensohler's (1988) steady-state charge distribution approximation was used to estimate the fraction of multiply charged particles contributing to the CPC number concentration for each diameter setting. There are a number of possible sources of uncertainty using these methods that may include particle losses, DMA transfer function uncertainty, counting uncertainty, and inversion errors. Consequently, the size distribution of particles selected at a particular voltage and flow setting of the DMA was examined using the UHSAS. UHSAS particle sizing is a function of the amount of light scattered onto the photodetectors. The quantity of scattered light, however, depends not only on the particle size, but also on the composition-dependent particle refractive index (Bohren and Huffman, 1983; Liu and Daum, 2000; Hand and Kreidenweis 2002; Rosenberg et al., 2012). The UHSAS manufacturer recommended calibration uses PSL microspheres, which are well characterized and have known refractive index ( $n = 1.58$ ) and shape. Because the UHSAS sizing is sensitive to particle refractive index, a new sizing calibration curve was produced for each studied particle type (i.e. refractive index) (Kupc et al., 2017). Considering this, we used the DMA, with sizing accuracy  $\sim \pm 2.5\%$  and NIST-traceable PSLs for 150 –500 nm spheres as our calibration standard. The UHSAS sizing was recalibrated by using the DMA to select particles of known size for each of the aerosol types studied. A different UHSAS calibration curve was produced and used for each aerosol type (e.g. Kupc et al., 2017). These calibration curves were used to retrieve accurate particle size distributions so that the multiply charged particles were properly accounted for. "

New text: *"For the liquid concentrations, atomizer conditions, and DMA settings used here, the DMA output size distribution was a multi-peaked population consisting not only of singly charged particles but also particles with multiple (mostly two or three) charges that can contribute significantly to the overall particle mass. Hence the particle mass could not be calculated directly from the singly-charged mobility diameter, particle density, and the CPC number concentrations. We generally used two methods to calculate the particle mass concentrations for these experiments. For the first method, the size distributions were measured using the scanning mobility particle sizer (SMPS; Wang and Flagan, 1990) function of the DMA (physical diameter,  $D_p = 1\text{-}1000$  nm). We used the DMA transfer theory (Knutson and Whitby, 1975; Stolzenburg, 1988) with Wiedensohler's (1988) steady-state charge distribution approximation to estimate the fraction of multiply charged particles contributing to the CPC number concentration for each diameter setting. There are a number of possible sources of uncertainty using these methods that may include*

particle losses, DMA transfer function uncertainty, counting uncertainty, and inversion errors. When comparing mass concentrations from the SMPS with those measured by the  $N_r$  system, issues with the SMPS-derived size distributions became apparent (discussed separately in Section 3.2.2). For the second method of calculating mass concentrations, we directly measured the diluted, DMA output using the UHSAS. UHSAS particle sizing is a function of the amount of light scattered onto the photodetectors, which depends not only on the particle size, but also on the composition-dependent particle refractive index (Bohren and Huffman, 1983; Liu and Daum, 2000; Hand and Kreidenweis 2002; Rosenberg et al., 2012). The UHSAS manufacturer recommended calibration uses PSL microspheres, which are well characterized and have known refractive index ( $n = 1.58$ ) and shape. Because the UHSAS sizing is sensitive to particle refractive index, a new sizing calibration curve was produced for each studied particle type (i.e. refractive index) using a DMA to select particles for a range of known sizes (Kupc et al., 2018). These calibration curves were used to retrieve accurate particle size distributions that properly accounted for the multiply charged particles. “

The following are additional areas of revised text:

P3 L17 We have eliminated the following text as it is repetitive: “~~By these methods, Roberts et al. (1998) confirmed efficient conversion of C1-C7 gas-phase compounds across the catalyst.~~”

P3 L30 We have eliminated the following text: “~~While these instrument calibration techniques are well established for controlled laboratory-generated aerosol standards,~~”

P4 L10-11 Existing text: “a particle-into-liquid sampler coupled directly to an electrospray ionization source and by the  $N_r$  instrument.” New text: “*the PILS-ESI/MS with that measured by the  $N_r$  instrument.*”

P6 L15-16 We eliminated the following text: “~~For purposes of this comparison, matrix effects were assumed to be negligible for tests sampling single component aerosols.~~”

P7 L35-37 We eliminated the following text: “~~For these reasons, we used the UHSAS size distributions to estimate the fraction of singly, doubly, and triply charged particles together with the total particle number taken from the CPC measurement to exclusive particle mass from total volume and density.~~” Then we added the following text to the end of the paragraph: “*Due to problems with measuring SMPS size distributions and requiring coincidence corrections for the UHSAS number concentrations, we used the UHSAS size distributions with the total particle number taken from the CPC measurement to calculate particle mass from total volume and density.*”

P10 L10-12 We eliminated the following text: “~~However, our results demonstrate the added challenges in particle mass determination using estimated size distributions from the SMPS method.~~”

P10 L12 We eliminated the following text: “~~Other aerosol measurement techniques (e.g. the Particle Time of Flight mode of the Aerosol Mass Spectrometer; DeCarlo et al., 2006) directly measure size distributions or instead measure polydisperse aerosol and the instrument and inversion algorithm corrections required using the SMPS are avoided~~”

And eliminate P18 L8-10: “~~DeCarlo, P. F., Kimmel, J. R., Trimborn, A., Northway, M. J., Jayne, J. T., Aiken, A. C., Gonin, M., Fuhrer, K., Horvath, T., Docherty, K. S., Worsnop, D. R., and Jimenez, J. L.: Field-deployable, high resolution, time-of-flight aerosol mass spectrometer, Anal. Chem, 78, 8281–8289, doi:10.1021/ac061249n, 2006.~~”

P12 L6-7 Existing text: “for the range of oxidation states. We are confident these results extend to other N<sub>r</sub>-containing particles, which is supported by the extensive list of N<sub>r</sub> gases efficiently converted as shown in Table 1. Therefore, we” New text: *“for the range of oxidation states and should extend to other N<sub>r</sub>-containing particles, we”*

P 12 L18-20 We have eliminated the following text: ~~“Initial tests with (NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub> proved more challenging as the low C number required large polydisperse aerosol loadings (several ppmv) to be measured reliably by the LICOR. During these instances, surface effects reduced the total N<sub>r</sub> signal, which likely resulted from NH<sub>3</sub> scavenging to the walls of the transfer lines or quartz tubing.”~~ And we combined the remaining sentences following this eliminated text with the above paragraph.

P12 L27-30 Existing text: “Here we demonstrate the capability of the total nitrogen system as an independent calibration method for aerosol measurement systems. N<sub>r</sub> measurements of laboratory generated single-component inorganic and organic aerosol particles were used to characterize a novel configuration coupling a PILS with electrospray ionization interface followed by mass spectrometric detection.” New text: *“Here we demonstrate the capability of the total nitrogen system as an independent calibration method for other aerosol measurement systems. N<sub>r</sub> measurements of laboratory generated single-component inorganic and organic aerosol particles were used to characterize the PILS-ESI/MS.”*

P12 L30-32 Existing text: “The strength of using the N<sub>r</sub> system to calibrate the PILS-ESI/MS is that it is a direct method to calibrate the entire coupled on-line system. The current calibration approach involves liquid-phase standards to calibrate the ESI/MS independently from the PILS.” New text: *“The strength of using the N<sub>r</sub> system to calibrate the PILS-ESI/MS and other aerosol mass instruments is that it is a direct method to calibrate the entire coupled on-line system. The current calibration approach for nearly all detectors used with the PILS involves liquid-phase standards to calibrate the detection method independently from the PILS.”*

P13 L6 We have eliminated the following text: ~~“In coupling an aerosol collection technique (PILS) with an electrospray ionization source, water soluble aerosol particles are speciated in real time.”~~

P13 L15-17 We have eliminated the following text: ~~“Because a greater aerosol particle mass could be realized by directly sampling the polydisperse output of the atomizer, our analysis focuses on comparisons between N<sub>r</sub> and PILS-ESI/MS without using the DMA size selection.”~~

P14 L30-32 We have eliminated the text: ~~“We evaluated this previously uncharacterized mass measurement technique using both traditional particle number size distribution measuring systems and the total N<sub>r</sub> mass measurement system.”~~ And added text “Here” to begin the following sentence.

P14 L33-35 We have eliminated the following text: ~~“Calibrating the ESI/MS using direct injection of liquid standards combined with mass concentrations collected by the PILS is a valid approach for quantifying inorganic components of aerosols, which likely extends to several organics as demonstrated by oxalate.”~~

P15 L2 to P14 L32 We moved the following sentence to an earlier section of the paragraph: *“PILS characterization has been limited to theoretical predictions or experimental comparisons that involve coupling the PILS with a mass analyzer (e.g. IC; Orsini et al., 2003; Sorooshian et al., 2006).”* And we added transition text: *“In general,”*

P15 L 3-5 We have eliminated the following text: ~~“Here we introduced a new method for calibrating the entire PILS-ESI/MS coupled system using  $N_2$  equivalent mass measurements of  $Cl^-$ ,  $NO_3^-$ ,  $SO_4^{2-}$ ,  $C_2O_4^{2-}$  from  $N_2$  containing particles.”~~

P14 L35 We moved the following sentence to an earlier section of the paragraph, existing text: “However, these ESI/MS calibrations are sensitive to the experimental conditions, which must be precisely maintained during ESI calibrations and throughout the entire sampling period. Changes in flow rate, interface positioning, or solvent composition have significant impacts on both the transmission and ionization efficiency ultimately effecting pre-determined ESI calibration factors.” New text: *“However, our current ESI/MS calibration methods are sensitive to the experimental conditions, which must be precisely maintained during ESI calibrations and throughout the entire sampling period. Changes in flow rate, interface positioning, or solvent composition have significant impacts on both the transmission and ionization efficiency ultimately effecting pre-determined ESI calibration factors.”*

#### **Exemplary technical comments:**

##### **P. 4, L. 3 should read “mass spectrometric detection”**

P4 L3 We added text: “*spectrometric*” between “mass” and “detection”

##### **P. 12, L. 20: should read “transfer lines”**

P12 L20 We have changed the existing text: “liens” New text: “*lines*”

##### **P. 13, L. 18: should read “Conventionally, : :”**

P13 L18 We added a comma “,” following “Conventionally”

#### **and other small mistakes, which should be considered upon revision of the manuscript**

There were a few other minor mistakes suggested by Reviewer 2 that we have corrected. Please refer to our response to Reviewer 2 for a few additional corrections. We have included below other small mistakes we have revised in the manuscript.

P2 L27 Existing text: “ $O_3$ ” New text “*ozone ( $O_3$ )*”

P3 L22 Existing text: “specifications” New text: “*design*”

P4 L4 Existing text: “calibrated using” New text: “*compared to the calibration obtained with*”

P5 L31 Existing text: “The PILS sample flow” New text: “*The PILS liquid outlet flow*”

P6 L28 Existing text: “atomization of” New text: “*atomizing*”

P6 L29 Existing text: “in a dry particle-free nitrogen flow” New text: “*in a dry particle-free nitrogen or zero air flow*”

P6 L29 We added the text: “*similar to the one reported by*”

P6 L31 We added the text: “*similar to one described by*”

P6 L33 We eliminated the text: “~~monodisperse~~”

P7 L1 We added a comma. Existing text: “output flow following dilution” New text “*output flow, following dilution*”

P7 L1 Existing text: “We measured the flow ” New text: “*We measured the CPC flow rate*”

P7 L37 Existing text: “exclusive” New text: “*calculate*”

P9 L15 We inserted additional text: “*on rapid timescales (a few seconds)*” following “However, the total  $N_r$  response precisely tracks the CPC signal”

P10 L14 Existing text: “Therefore, we instead” New text: “*Here we*”

P11 L1 Existing text: “ $N_r$  measurements of biomass burning” New text: “ $N_r$  measurement of biomass burning emissions”

P11 L33 Existing text: “ambient air is eliminated” New text “*ambient CO and CO<sub>2</sub> is eliminated*”

P12 L21 Existing text: “ $N_r$  system” New text: “ *$N_r$  catalyst*”

P13 L3 Existing text: “measurements of nitrate” New text: “*measurements of ammonium salts of nitrate*”

P13 L7 Existing text: “through” New text: “*using*”

P15 L8 We eliminated the text “~~monodisperse~~”

P15 L31 Existing text: “demonstrated that this technique” New text: “*demonstrated that the  $N_r$  conversion technique*”

P15 L33 Existing text: “of” new text: “*within*”

P16 L28 We eliminated the text “~~airborne~~”

P17 L27 We capitalized the text: “aerodyne”

P18 L28 Existing text: “P. Natl. Acade.” New text: “*Proc. Natl. Acad.*”

P27 L4 Existing text: “commercial” New text: “*custom*”