Response to Reviewers for:

Modification and validation of a commercial dynamic chamber for reactive nitrogen and greenhouse gas flux measurements

Moxy Shah, Kifle Aregahegn, Danial Nodeh-Farahani, Leigh Crilley, Tasnia Hasan, Yashar Ebrahimi-Iranpour, Fahim Sarker, Nick Nickerson, Chance Creelman, Sarah Ellis, Alexander Moravek, and Trevor VandenBoer

General Response

We would like to thank both Reviewers for taking the time to review our manuscript and to provide thoughtful and thorough feedback on our work. We feel that the changes to this manuscript based on their comments makes our work stronger, and more widely accessible to the atmospheric research community. While we have worked hard to reduce the length of all sections of this manuscript and have performed a complete edit of the work for concision. We have removed a full page of text between the abstract (17 lines) and introduction (25 lines), nearly two pages from the methods (49 lines), and almost two pages from the results and discussion (57 lines). Some information has also been moved to the SI (~2-3 pages).

We have also provided clarifications throughout the manuscript with respect to chamber closure duration tradeoffs and the surface-interaction term, λ, used to conduct corrections. As the overall response is quite long, we have tried to limit repetition of those changes and refer Reviewer 2 to the responses we have made to Reviewer 1 where there are substantive overlapping concerns. We hope the Reviewers find we have approached our revisions with care and that this work is now acceptable for publication in Atmospheric Measurement Techniques.

Below, please find our point-by-point responses to the comments from each Reviewer indicated with '**Response:**' and the text provided with *italics formatting*. Where we have made changes to the manuscript, we indicate it with '**Modification:**' and provide the lines of text in the tracked changes manuscript with yellow highlighting and revisions therein with **bolded formatting**.

Referee #1

Summary:

This manuscript details the experimental design, configuration/modifications, and utility of a dual system of commercial dynamic chambers for simultaneously quantifying emissions fluxes of reactive nitrogen species and greenhouse gases. This work carefully outlines the system details as well as the many considerations that go into the flux calculations, which are further described in the context of a proof-of-concept experiment aimed at quantifying emissions fluxes of nitrogen species and greenhouse gases from agricultural soils. This manuscript is a highly valuable addition to the literature because it provides: 1) a description of the dual-chamber system detailed enough for others to reproduce, 2) a comprehensive account of the considerations and calculations needed for dual-dynamic chamber flux calculations, and 3) initial proof-of-concept results from controlled laboratory and field experiments. The latter shows great promise in being able to set a foundation for charactering changes in emissions fluxes of nitrogenous species and greenhouse gases from agricultural soils as a function of relative humidity, temperature, soil moisture, fertilizer applications, and more, which are critical for understanding emissions from food systems that impact air pollution and climate. This manuscript is well written, and it fits well into AMT. I recommend this manuscript for publication. Please find a few minor comments and suggestions below.

General comments:

While this paper is very comprehensive, a missing component of this work seems to be a **brief, clear, and upfront discussion of the advantages of this dual-dynamic chamber system compared to the system described in Pape et al., 2009**, who also implemented a blank chamber in reference to up to as many as 6 sampling chambers and measured Nr species. It would strengthen this work to be more explicit about the novel aspects of this dual-dynamic chamber system and proof-of-concept experiments in comparison to the dynamic chamber system and field measurements described in Pape. This could be integrated into the last 1-2 paragraphs of the introduction.

Response: *We thank the Reviewer for this comment and agree that we can expand on the advantages of this modified chamber system, namely the assumption that local sources are not changing the ambient quantities of Nr dramatically during the measurement period, but also that the gas handling is simplified, following standardized greenhouse gas flux techniques (hence the appealing nature of modifying a commercially available chamber). We are also able to comment on the quantity of gas flowing through the headspace later in the manuscript, to address their additional comments below. We have made the following addition to the introduction, as they have suggested.*

Modification:

Lines 196-233, Introduction:

“Thus, establishing an accessible dynamic chamber method for N_r flux measurements is desirable. However, such a platform needs to undergo extensive validation to reduce flux bias from challenging N_r species such as NH_3. This important and necessary first step will allow a wider global study of surface-atmosphere N_r exchange processes. **One of the best existing examples to date of automated dynamic chamber design for N_r measurements, is the custom-built system from Pape et al. (2009) who measured NO, NO_2, and O_3 to deploy an unattended array of six**

samplers with destructive gas analyzers. In their system, a reference chamber was used to characterize system surface effects, while using a large volume flow through the headspace during chamber closure periods to quantify fluxes on the assumption that ambient levels were not dramatically changing (e.g. due to nearby point sources). This work synthesized many advantages from similar designs to study soil- and plant-atmosphere interactions, but the technique remains accessible only to researchers with in-house engineering design and fabrication facilities. In the intervening years, dynamic chambers for GHG fluxes have become widely commercialized to improve measurement capacity compared to static chamber determinations and to make flux observations more accessible compared to conducting eddy covariance measurements.

Here, we **bridge several gaps to link the atmospheric GHG and N_r flux communities to yield a dynamic flux system for CO_2, CH_4, N_2O, NO, NO_2, HONO, and NH_3. First, we** modify commercial dynamic chambers **with large volume (72 L) and footprint (0.21 m^2)** originally designed for **trace** GHG flux measurements to make them suitable for quantifying the most prevalent N_r gas exchange fluxes at surface-atmosphere interfaces**, meaning the apparatus is more widely available to the atmospheric community. Next,** we implement surface and hardware modifications to adapt the commercial chambers to minimize gas adsorption and transformations**, so that more reactive gases such as HONO and NH_3 can be added to the N_r flux analyte suite.** We systematically characterized the transfer of both GHGs and N_r species by calculating fill and empty rates, transformed to time constants, to identify any surface interactions and/or transformations on the chamber surfaces. We then applied our modified commercial dynamic chambers to make flux measurements by equipping them with destructive gas analyzers for HONO and NO_x and a cavity ring-down spectrometer (Picarro G2509) for NH_3, N_2O, CO_2, and CH_4 in lab experiments, or with a fully automated dual-chamber approach under field conditions through a pilot study **with 30 minute closures to obtain a sufficient number of measurements to detect relevant fluxes with standard gas analyzers. Fluxes during the pilot study were assessed by rate of change determinations during closure periods and** bias minimized through a mass balance **to demonstrate system capabilities** for several N_r gases **in an agricultural field**. This community-accessible approach addresses key needs by allowing more researchers to measure N_r exchange at the surface-atmosphere interface, with **the added benefit over past systems** to monitor fluxes of all species simultaneously with at least hourly time resolution **when using gas analyzers with one-minute measurement frequencies**."

At first look, the 30-minute sampling cycle for the MC and RC chambers seems a bit short. On the other hand, a longer sampling time probably allows for more dilution, reactivity, etc. It seems like there is a delicate balance of the time to observe enhancements in the chamber, trace gas analyzer response times, chamber flush times/flow rates, dilution times from the replacement make-up gas, and the time associated with wall loss in the chamber, etc. **Is it possible to combine all of these timescales into a single schematic to demonstrate this balance? Is there a sweet spot in the**

schematic that clearly stands out for this set up? At a minimum it might help to add some more detailed explanation about why the chamber time to reach a reasonable detection limit for HONO (e.g., Section 2, L250) is used compared to the longer chamber fill/empty time for sticky NH3 (e.g., Figure 2 and Table 1). How would using a different chamber sampling time impact your flux results? It seems like a good bit of the chamber timing characterization was also discussed in Pape et al., 2009 (e.g., their figures 6 and 7). Briefly summarizing the timing simulations in Pape with respect to your timing scheme could help clarify and strengthen this work.

Response: *If anything, our 30-minute sampling time is too long and could be shortened where fluxes are modest or when destructive gas analyzers with higher time resolution than 1 minute are at hand. For example, in the Pape et al. work the Reviewer asked us to contextualize above, their* NO_x *analyzer had 20 s time resolution, which means a sufficient number of data points could be obtained from 4-minute intervals of ambient-chamber-ambient air samples, for a total flux determination time of 12 minutes, inclusive of discarded data from valve switching and associated gas exchange.*

Their timing requirements considered in Figures 6 and 7 are used to set the discarded data intervals in the ambient-chamber-ambient cycle. This means their timing considerations are different from ours, as their observations require a steady state concentration from a constant flux to be reached inside the chamber, with the flux determined by difference from the ambient observations. In contrast, we determine fluxes by a rate of accumulation or loss determined during the observation/chamber closure period, following the validated design commercialized by Eosense Inc. (and others like Licor). Our closure duration in this work is set mostly by the need to collect enough data points to characterize this rate sufficiently by linear regression. Since our standard gas analyzers have a measurement rate of once per minute, we obtain ~20 observations to determine a flux per closure period after discarding boundary observations, following a similar rationale to that of Pape et al. A more detailed presentation and optimization of the flux determinations is planned for inclusion in our forthcoming manuscript that presents the 2 weeks of our field observations in detail.

In any case, the only core requirements here are i) obtaining enough observations to conduct a reliable regression on the concentration change over time, and ii) sampling at as low of a flow as possible to minimize changes in the headspace composition from ambient. Our only timing optimization in this work was centred on accumulating enough of the N_r *species to get a reliable determination. This means we focused on the* N_r *gas with the highest uncertainty in its fluxes from the perspective of atmospheric chemistry, which was nitrous acid (HONO). There are widely varying reports of its flux magnitude, and with a 30 minute closure interval, we calculated that it would be easy to measure emission fluxes at the lower limit of those reported by others – an estimate that we have placed poorly in the current manuscript and need to present the rationale for sooner, as the Reviewer has noted.*

As field-based HONO fluxes are also much smaller in magnitude than the remaining N_r gases, the trace nature of HONO essentially sets the method detection limit and thus the upper boundary of the chamber closure duration, a consideration which we will aim to clarify through a concise revision.

Lastly, this also means the 30-minute closure is more than effective for NH_3 despite its surface activity because it is much more abundant, by up to two orders of magnitude compared to HONO, so the longer response time has a trivial impact on our capacity to quantify the fluxes (e.g. see the discussion around uncertainties in Section 3.3.3). Also in our forthcoming publication that presents the full dataset from our field observations, we are planning an expanded discussion of the system detection limits that result from the 30-minute closure period and find them to be well below the range of previously reported fluxes, e.g., method detection limits of 0.216 nmol m^{-2} s^{-1} for HONO and 0.0456 nmol m^{-2} s^{-1} for NH_3 for a 30-minute closure period, both of which are roughly one order of magnitude lower than fluxes reported in the literature (again, see Section 3.3.3 for discussion of prior N_r fluxes measured in the main manuscript).

Given the current length of our manuscript (an item which both Reviewers requested we try to address through shortening sections), we have implemented a few small changes to clarify why the 30-minute closure period was selected and is sufficient. As our principle for flux determination is different, we have opted to exclude a compare and contrast statement with respect to the work of Pape et al. as this may introduce additional confusion on our approach. Instead, we have introduced changes that discuss the benefits and drawbacks of longer or shorter observations periods in relevant locations within the discussion and some contextual guidance in the conclusions, as well as adding a second panel to Figure S11 in the SI to show the effect of closure duration on λ values for surface-active gases.

Modification:

L282-290, Methods, Section 2.1.1:

"Thus, the measurements are taken every 30 minutes, where one chamber is closed for gas analysis while the other is open to the ambient atmosphere. The sampling time interval was determined based on **i) obtaining enough measurements at 1-minute time resolution to perform a reliable accumulation or loss linear regression, and ii) an ability to readily detect** the lower limit of the range of field HONO flux values reported in the literature to ensure detection in its application during our pilot field study (see Section 2.7). **For the first criterion, this also includes an exclusion of the first few measurements (3 to 5) to allow for complete gas replacement between the chamber lines and the analyzers, and disruption of the sealed environment as the chamber cycle alternates, respectively.**"

L1090-1101, Results and Discussion, Section 3.3.3 on pilot field study:

"For the 0.5 Hz measurement rate of the Picarro, it is clear from the accumulation and depletion of target gases in Figure 5, that a shorter observation period than 30 minutes could be used when high time resolution instrumentation across all target species is available. The benefit of this would be to reduce both the alteration of the composition of the chamber headspace and diverging physical conditions between the chamber and ambient environment; ultimately obtaining better flux estimates. However, for this pilot study, the 1-minute time resolution of the NO_x analyzer and the method for determining HONO by difference with an annular denuder every 5 minutes required the 30-minute interval. A shorter closure period could also have the drawback of worse flux detection limits when fluxes are small, and more variability due to a less robust regression of the accumulation or depletion rate. For example, this would increase the value of λ for NH_3 (Figure S11; Section S7) and its relative error (4% for a clean system, Section S7.3) as well as other surface-interacting gases."

L1297-1301, Conclusions:

"The duration of the chamber closure for the modified NO_x analyzer used in this work made a 30-minute observation necessary to obtain sufficient measurements for a reliable flux determination. Use of higher time resolution gas analyzers can readily reduce the observation period and continue to produce reliable fluxes, depending on the flux detection limit desired, and tolerance for inflated surface effects."

Figure S11:

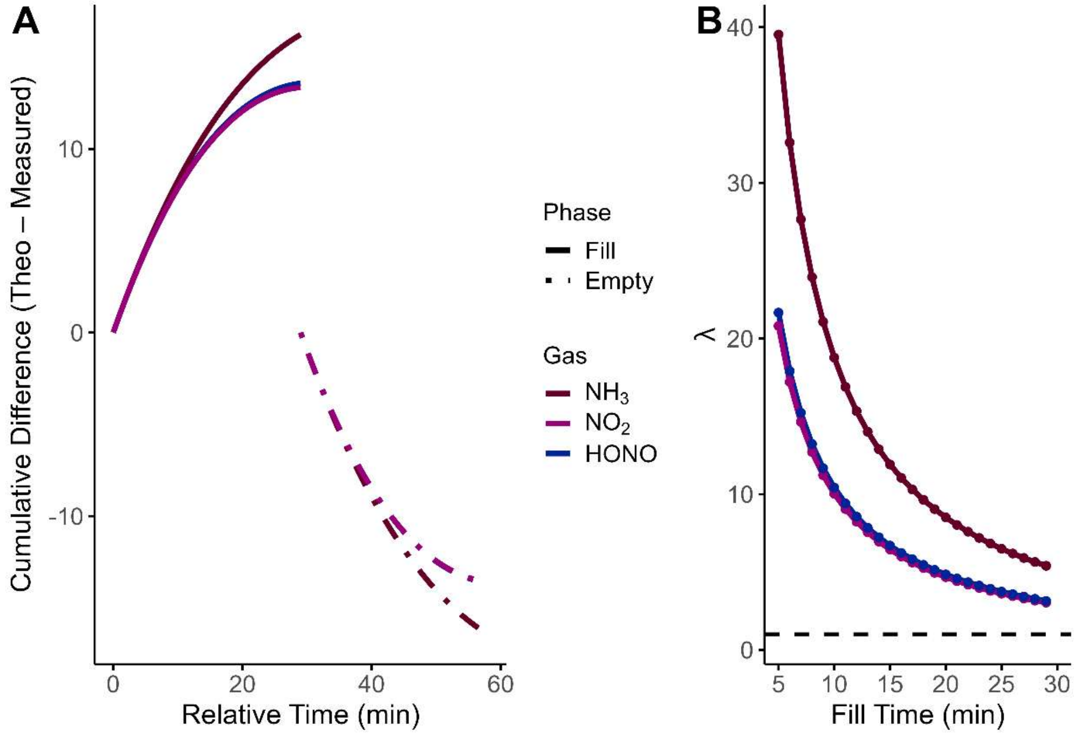


Figure S11. (A) Cumulative integration of the difference between **inert** and measured gas concentrations for NH_3, NO_2, and HONO over a 30-minute filling and emptying period **and (B) resulting λ values for modified chambers, 15 m PFA lines, and gas analyzers as a function of filling time with a dashed line at one corresponding to the transmission of an inert gas.** Theoretical concentrations represent expected values **from an inert gas** without attenuation, while measured values reflect signal loss due to gas–wall interactions. Solid lines correspond to the filling phase; dashed lines represent the emptying phase, together representing a full in situ measurement cycle. These illustrate the time-dependent and nonlinear attenuation that underlies the empirical calculation of λ. **Note that due to observations switching to the RC, the emptying phase does not impact the value of λ applied during field use.**

This paper is well-written and comprehensive. However, it is a bit cumbersome in places. **A suggestion for improved readability could be to reconsider what goes in the main paper vs. the SI. For example, Section 2.1.2 seems better suited for the SI, while important analyzer calibrations and gas handling considerations are handy to have in the main paper**. Similarly, important equations and calculations, such as those in Section S7, while cumbersome for the main paper, could go into an appendix of the main paper for increased visibility.

Response: *We thank the Reviewer for their feedback here and we also greatly struggled to balance the information that is most relevant into the main manuscript and which belongs more in the SI.*

As they also have expressed similar conflicting ideas, we have opted to identify alternatives for shortening the length of our manuscript.

We agree with the identification of Section 2.1.2 being partially moved to the SI and have relocated 5 lines of text, but the remainder of the information here is a novel design that needs to remain in the main manuscript.

With respect to the suggestion of creating an appendix for the main manuscript, we do not agree on this as AMT is an open access journal, which means that both the manuscript appendix and SI are equivalent forms of documentation accessible to our readers.

Modification:

In the end, we have decided to fully edit the manuscript to reduce the reading encumbrance of as much material as possible and found that it was possible to remove approximately 7-8 pages of material from manuscript in full as well as relocating 2-3 pages of material to the SI (as noted in our general response above). We hope this substantial revision to improve clarity, reduce repetition, and focus the manuscript on the main findings meets the Reviewer's expectations.

Specific comments:

L183: Suggest changing "manipulated" to "performing controlled experiments"

Response: *We agree with the Reviewer and have implemented this change.*

Modification:

Lines 193-196: 'Automated dynamic chambers deployed in situ for field observations **and performing controlled experiments** would provide a platform for capturing the magnitude, direction, and temporal variability of N_r species or physical variables via the headspace gas or soil amendments while retaining soils in an intact state.'

L250: Is there a reason that HONO is used to determine the sampling time interval, compared to say NH3? Section 2.6 did not seem to provide further explanation for this selection. Is this somewhere else? At a minimum, this section seems like a good place to summarize some of the chamber timing simulations in Pape et al., 2009. It would also be a good place to discuss similarities and differences in timing between your experiments and their studies (e.g., differences in timing with respect to differences in flow rates).

Response: *This comment has been addressed in a prior response above, as this same issue was raised by the Reviewer earlier.*

L279: This should be Section 2.1.3, right?

Response: *We thank the Reviewer for catching this typo. We have corrected the cross-referencing section numbering.*

L281: Section 2.1.2 seems like it could go in the SI, and then the instrument descriptions can naturally follow on Section 2.1.1.

Response: *Parts of this section are novel and fundamental to the valve switching used in our pilot study, so we could not move it entirely to the SI.*

Modification:

We were able to relocate 6 lines of text from this section to the corresponding one in the SI.

L305-317: Can you determine an analyzer detection limit for HONO?

Response: *Yes. Absolutely. It is identical to that for NO_2 when using the scrubbing denuder. The following sentence has been added for further clarification in this section.*

Modification:

Line 343-345:

"The calculated LOD determined from sampling dry zero air was 0.84 ppbv, 0.67 ppbv and 1.07 ppbv for NO, NO_x, and NO_2 **(or HONO when using the denuder as described below),** respectively."

Section 2.1.3 and L309: Did you actually measure interferences from other oxidized nitrogen species in the NO2 measurement?

Response: *We are not entirely sure which method of measuring interferences the Reviewer might be referring to here, as it could be lab characterization of the system, lab-based soil experiments, or field observations. If they are asking if we performed NO_y standard addition experiments to the NO_x analyzer, then the answer would be no for any NO_y species except HONO, as there are prior reports in the literature that we have cited describing the previously determined interferences.*

If they are asking if we independently found other NO_y species being emitted from our soils, and if those NO_y happen to also have been reported as interferences, then the answer to that would also *be no. For the purposes of this work, the capabilities of our system were focused on emissions rather than deposition, partly due to the limitation of our modified NO_x analyzer approach, as we expect interferences like HNO_3, PAN, or N_2O_5 to only deposit in these systems, and HONO would be the major interfering species expected to be emitted. We acknowledge that this is a limitation of this measurement approach and our plans initially included use of our time-of-flight chemical ionization mass spectrometer (ToF-CIMS) to have more definitive speciation throughout this work, as well as to include more presentation of deposition determinations. Due to manufacturer issues with this platform it was not possible to do so at the time. As these issues are currently fixed, we plan to use the ToF-CIMS to conduct speciated measurements that overcomes this ambiguity in the future. We have made a few minor changes here and in other locations throughout the manuscript to clarify this limitation and how it might be overcome with a better tool like the ToF-CIMS.*

Modification:

L348-360, Methods:

'To prevent interferences **reported by others** from atmospherically-relevant acidic species in this system (e.g. HONO, HNO_3, and N_2O_5) the sampled air from the chambers during field experiments was passed through a sodium carbonate (Na_2CO_3) coated annular denuder to reduce bias in the NO_2 measurement, as these species and other components of NO_y (e.g. peroxyacetyl nitrate; PAN) may also be reduced to NO (Villena et al., 2012). The Na_2CO_3 denuder was prepared according to the EPA Compendium Method IO-4.2 (Winberry Jr et al, EPA, 1999) to remove atmospheric acids by reactive uptake to the basic coating. As part of our controlled laboratory and pilot field study experiments, this denuder was also used to selectively measure HONO by scrubbing this target gas for a specified period**, but would include the other known interferences. If this term is depositing, it could include the other NO_y detected by the same conversion mechanism, but if emitting we expect it to be dominated by HONO. Ideally, a platform like time-of-flight chemical ionization mass spectrometry (ToF-CIMS) would be used for disambiguation but was not available at this time.**'

L1322-1324, Conclusions:

'We show here, for the first time, that such a system can provide simultaneous measurement of NO, NO_2, HONO, NH_3, CO_2, H_2O, CH_4, and N_2O fluxes. In addition, we show fully automated operation of the chambers, switching of sample flows, and data collection workflows for continuous and unattended measurements of fluxes at field sites. **Ideally, modern instrumentation like the ToF-CIMS would be coupled with this system to shorten the chamber closure duration, and better distinguish HONO from other NO_y fluxes, instead of a modified NO_x analyzer.**'

L329: The Picarro **analyzer response times** are given as 8 s for non-sticky species, which are assumed to be 1/e times of a single exponential function. While this seems sufficient compared to the chamber empty/fill times for non-stick species, the longer analyzer response time for sticky NH3 (reported as <2 min) may rival the chamber fill/empty times (e.g., Table 1) when a double exponential fit and a longer, more appropriate, signal recovery time (e.g., t90, the time for 90% signal recovery) for sticky molecules are considered. Can you comment on this?

Response: *The NH_3 analyzer response time is more than sufficient for quantifying the fluxes and, to our knowledge, corresponds to a t95 or higher. Regardless, it is a factor of 20 faster than the response times we report in Table 1, which are dominated by the chamber and gas transfer line surfaces. The issue is accounted for through the use of the λ value introduced in this work, as its determination includes the surface interactions of NH_3 with both chambers and the analyzer. We have clarified this in the methods section where we present this term as part of its definition.*

Modifications

L607-608, Section 2.6:

"The dimensionless attenuation factor λ is required to correct for interactions of reactive gases with chamber surfaces."

Is now:

"The dimensionless attenuation factor λ is required to correct for interactions of reactive gases **with surfaces.**"

We have likewise revised 'chamber' to 'surfaces' and added at L594-598:

"The RC captures environmental fluctuations such as temperature or pressure change and directly observes the interactions of ambient gases with surfaces within the sampling setup **(i.e. chambers, gas transfer lines, valves, and analyzers)**, as well as tracking reactions, allowing for corrections to every net flux (F_{net}) measurement cycle (E6 for reactive gases and E7 for non-reactive gases, as derived in Section S7)."

And at L609-615:

'Thus, λ is derived as the ratio between a theoretical unattenuated gas **(i.e. an inert GHG like N_2O)** and the target gas concentration from controlled deliveries integrated over the chamber closure interval as derived in Section S7. **This term has the surface effects from chambers, gas transfer lines, and analyzers embedded by definition and must be determined empirically for any altered configuration.** The attenuation correction removes bias from **surface**-induced artifacts in flux estimates, so that more accurate soil–atmosphere exchange is reported.'

And more generally for surface-interacting gases at L660-663; Section 3.1.2:

"The slower time response of the NO_2, HONO, and NH_3 measurements is determined by two processes: (1) the exchange of the sample air volume **in the gas transfer lines** and the chamber, and (2) the adsorption and desorption of the gas onto and **from their surfaces** (Whitehead et al., 2008)."

While the chamber response times are well-addressed in Section S3, it was not obvious how the analyzer's response times are characterized for stick molecules (NH3 and HONO). What is the modified NOx analyzer's response time for the HONO measurement and how is it defined?

Response: *We have previously characterized the modified* NO_x *analyzer's response time for HONO to be faster than the 1-minute measurement time resolution (Lao et al., 2020). That work has been cited where appropriate in this manuscript. Throughout this work, we were not substantially impacted at any point by the analyzer response times relative to the surface effects introduced by the chambers (if any) and those reported in the descriptions are therefore all that are necessary to provide. We have made a small addition to the Picarro description to be clear on this (see changes indicated in the next response), as well as the modifications to clarify that our chamber characterizations are inclusive of analyzer response times in the preceding response.*

Another consideration is whether the time responses of these analyzers and the chambers were characterized multiple times throughout the study period to ensure that they did not change. The time response of instrument systems measuring sticky molecules are well known to degrade over time and usage as sampling surfaces get dirty or saturated with moisture (e.g., Ellis et al., 2010; Moravek et al., 2019; Roscioli et al., 2016, https://pubs.acs.org/doi/10.1021/acs.jpca.5b04395, etc.). How might changes throughout the study period in analyzer and chamber response times for sticky molecules impact your results? Some additional discussion could help clarify. (See also additional related comments below with respect to lambda.)

Response*: All of our analyzers have filters and heated cavities to prevent the effects being described here by the Reviewer. We did not observe any noticeable changes in the instruments' performance with respect to response times throughout our work. This has been clarified with a small addition at the location noted by the Reviewer. The works cited here for* NH_3 *are reporting changed performance with respect to the degradation of air sampling inlet materials, not the interior of the instrumentation itself. This matches the common mantra for low volatility gas sampling where 'your measurement is only ever as good as your inlet'. We reported the impact of the chamber surfaces degrading with the transfer of ozone and have been clear that the effect was substantial, but this included years of use and was not systematically isolated.*

In our lab experiments, the chamber surfaces were kept clean to prevent this effect. In the field, our observations were done under such hot conditions that surface effects for NH_3 were reduced just due to the physical conditions at the field site. With the fertilization experiment producing enormous NH_3 mixing ratios (>1 ppmv,) surface effects would introduce a trivial bias on mass transfer and determined fluxes as they are a constant loss by adsorption, not proportional. So, for the data presented in this manuscript, we feel confident that surface aging and mass transfer hysteresis effects are minimized. We now provide further cautionary instructions for the community on anticipating this effect and have made a small addition in the Conclusions.

We also do have the capacity to comment on this from a more recent 6-week deployment of this system under much more challenging circumstances (i.e. high winds, intense rain, cold, hot, and highly variable humidity/dew; Figure R1). In that deployment, we simply looked at the decay of NH_3 in the reference chamber while it is diluted as an indicator of increased surface aging and mass transfer issues. We found that the surfaces do develop stronger hysteresis over time, particularly with very wet conditions, such that the transfer of NH_3 would be attenuated to a greater extent. To account for this would require the performance of NH_3 standard addition to the headspace of the reference chamber to track the changing value of lambda over time.

The stronger interactions would mean that the lambda value increases as the surfaces age, so using a value for a clean system will provide a reliable lower limit determination of NH_3 fluxes, but where substantially aged surfaces are involved they will be biased low if a correction mechanism is not used. As the Reviewer can appreciate, with the length of the current manuscript, we are going to reserve this information on system performance optimization in the field for our forthcoming manuscript.

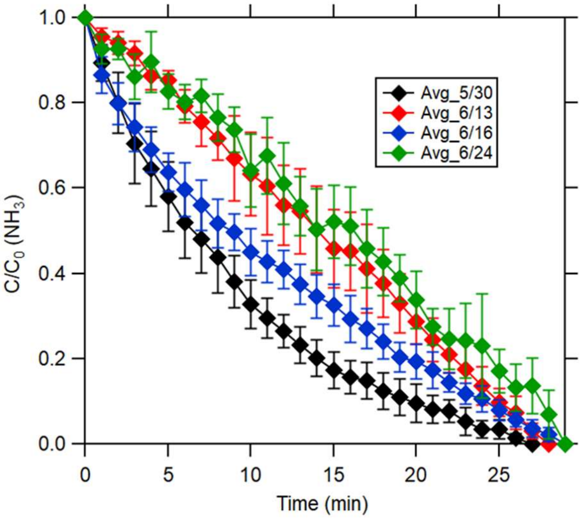


Figure R1: Normalized decay of NH_3 when observing the reference chamber surface at timepoints throughout a subsequent 6-week campaign showing changes in attenuation, with a trend towards a slower decay by end of the observation period. Each trace is the average of 6 hours of observations from a given campaign day with a single standard deviation defining the error bars.

Modifications:

L379-380, Methods, Section 2.1:

"The instrument cavity material was treated with a SilcoNert® coating by the manufacturer. **We did not observe changes in its performance for the measured gases when operated according to the manufacturer guidelines.** The Picarro G2509 analyzer **spectroscopic mixing ratio determination means** a full span calibration **is not a regular necessity**. Despite this, we validated its calibration and performed quality control checks in **the lab** to ensure the accuracy and stability of the analyzer for all aspects of this work (Section S2)."

L1305-1309, Conclusions:

"**One further limitation is that the chamber and gas transfer line surfaces may accumulate material and change the mass transfer of gases, particularly NH_3, over time. This effect can be monitored using the reference chamber if sufficient quantities are present in the ambient air, via the dilution decay rate and characterized in situ by a standard addition of the necessary gases to the headspace.**"

L337: I agree that full span checks for greenhouse gases are not regularly needed for the Picarro, but I'm not sure that holds true for sticky NH3. You mention performing regular calibration checks anyway, which is good. How often were those performed? Did you observe changes, or more variability, in the NH3 channel? How about checks of the instrument time response, especially to NH3? Did that time response change over the duration of your study?

Response: *We appreciate the concern of the Reviewer. As noted in our response above, the response time of the Picarro analyzer is approximately a factor of 20 faster than the temporal resolution used for flux quantification and therefore does not limit the flux calculations. In addition, the Picarro analyzers are equipped with a heated sampling cavity and operate at lowered sampling pressure, both of which reduce gas adsorption and minimize wall interactions within the analyzer. Span checks were performed before and after each experiment, as well as the 2-week field campaign, and no significant variability in* NH_3 *response was observed. This suggests no measurable change in analyzer response time was introduced during the field sampling, as per the instrument design. As this type of characterization is embedded in operating manuals for such systems by the manufacturer, we have opted to make only the small change noted above to the manuscript, as we did not see any issues with* NH_3 *detection performance when following those guidelines.*

Related details about analyzer calibrations (in the SI) could also be clarified. Specifically, how was the modified NOx analyzer calibrated for HONO and how was the Picarro analyzer calibrated for NH3. This should be added to Section S2 if different from the methods used to characterize the chamber time response measurements in Section S3. If they are the same, it might be clearer to add the calibration procedure to section S2 and then refer to it in section S3.

Response: *This is our mistake and the Reviewer is right that the calibrations should all be collected in one location. Details of the calibration procedures for HONO and NH_3 have been moved and are now described in Section S2, as they have suggested and read as provided below.*

Modification:

Lines 83-94, Section S2:

"The criteria for a successful calibration are the same as described for NO. Conversion efficiency (CE) of NO_2 to NO in the analyzer is the final parameter to be quantified, and a CE > 96% indicates that the molybdenum catalyst in the analyzer is operating reliably.

Nitrous acid (HONO) was generated using our in-house calibration source based on the reaction between gas-phase hydrochloric acid (HCl) and a $NaNO_2$ crystalline film on the surface of PFA tubing (RS-1) at 50% RH to generate gas-phase HONO and to confirm its unity conversion (Lao et al., 2020).

$$NaNO_{2(s)} + HCl_{(g)} \rightarrow HONO_{(g)} + NaCl_{(s)} \qquad \textbf{RS-1}$$

In the HONO calibration source, a flow of dry carrier gas (Air Ultra Zero, 99.999%, AI 0.0UZ-K, Praxair) at 50 cm^3 min^{-1} passes through a permeation device (PD) containing HCl solution, heated to 30-40 °C. Another 50 cm^3 min^{-1} passes through a glass impinger containing deionized water to become saturated with water vapour, so the flow obtains an RH of 50% when combined with that of the HCl. This HCl-water vapour mixture enters a $NaNO_2$-coated PFA reaction device, and HONO is released by acid displacement. A delivered mixing ratio of 10-100 ppb was found to be effectively converted, in line with the performance we have previously described in detail."

Line 103-114, Section S2:

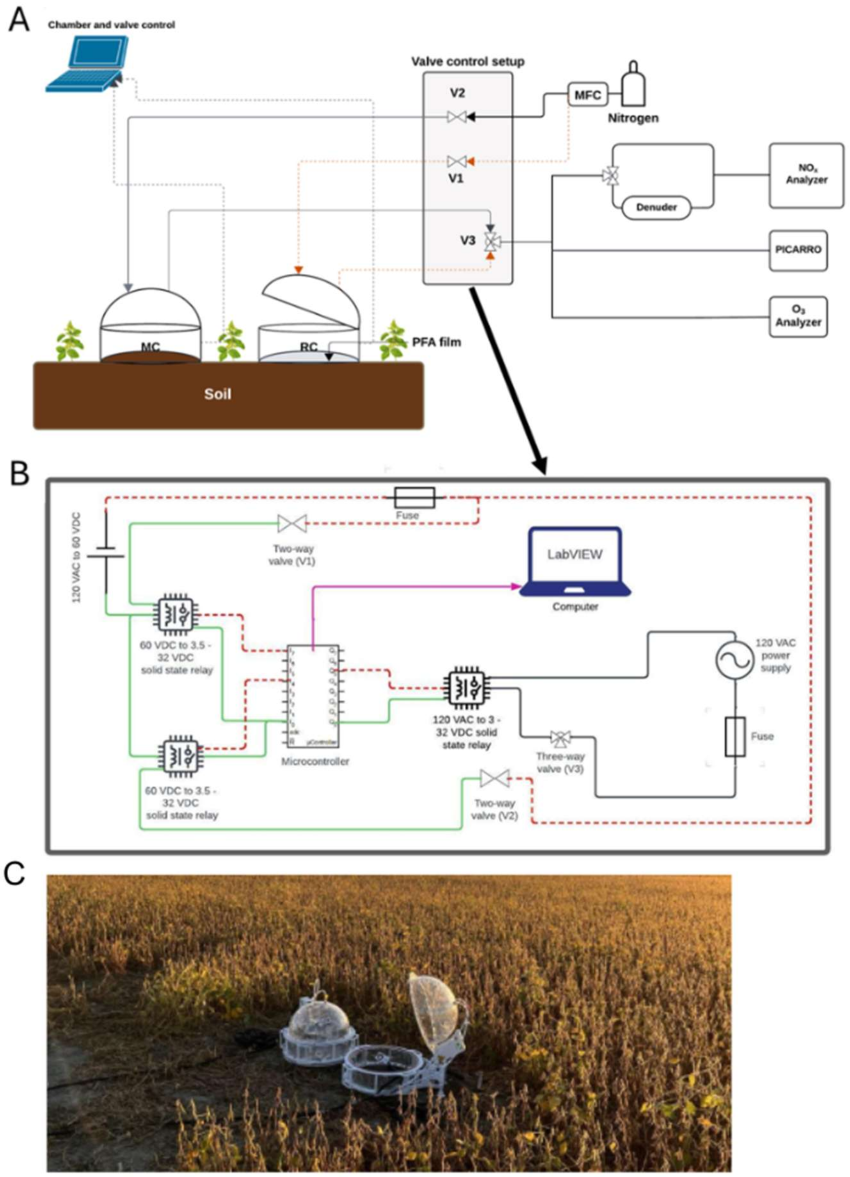
"Pure nitrogen and three calibration points at none, 4.5, and 10-times dilution of the original GHG mixing ratios in the cylinder were delivered to the Picarro analyzer until stable responses were achieved, in triplicate**. The custom-built permeation oven for HONO was also used to generate known mixing ratios of NH_3 by quantification of bubbler-scrubbed NH_3 using ion chromatography (Salehpoor and VandenBoer, 2023). A dry 90 cm^3 min^{-1} zero air flow was passed over a PD containing NH_4OH (30% v/v in 1/8" OD tubing with a 9 cm length). Calibration was performed for mixing ratios of 30 ppbv to 110 ppbv.** The dilution of gases was achieved by combining the flow from a liquid N_2 dewar (Linde Canada Plc, PN: NI LC250-230). The observed versus returned slopes of 0.99 for N_2O, 0.99 for CH_4, 0.98 for CO_2, **and 1.37 for NH_3** when compared to the known concentrations delivered, thereby demonstrating suitable and stable calibration of the instrument, as these slopes are within the cylinder **or IC** mixing ratio uncertainties."

L354 and Section 2.2: It would help to see a photo of the chambers in the lab or in the field in the main paper in this section. Maybe a photo of the chamber set up in the lab or field (like in Figure S2 - very cool!) could be added to Figure 1 as a part C in the main paper?

Response: *Thanks for the suggestion! We definitely have a collection of photos of the system in action in the field and have added one as a panel in Figure 1, as suggested.*

Modification:

We have updated Figure 1 and added the description for the panel below to its caption.



“(C) Field deployment of the dynamic chamber system, where the closed chamber is the reference and the open chamber functions as the measurement chamber.”

The PFA film over the lid is a smart addition to reduce surface interactions. Is the air sample completely isolated from the polyacrylate cover (aka. is there a leak-free seal between the PFA film and the cover)? If not leak-free, does the adhesive on the double-sided sticky tape create any chemical interference?

Response: *Thanks for the compliment! Ideally, this film would be gas-tight, but it is not. We also considered the application of a surface coating that retains optical transparency yet we could not find a product capable of doing this that doesn’t make the chamber lid optically opaque in the visible region, reducing its capability to contain growing plants, and preventing the option to replace it after it ages. Pursuit of a replaceable gas tight PFA film option on all chamber surfaces is still something we are exploring from an engineered perspective now that we have solid proof of the system benefits.*

Overall, we were surprised that the N_r *reactivity could be reduced across the board despite the lack of gas-tight seal. We expected the tape to potentially create some issues, but did not find any for even our worst behaving gas,* NO_2*, nor any of our other target* N_r*. This may be good luck for this compound class, as it may not be the case for other volatile organics and could partly explain our* O_3 *loss in the pristine PFA film version of the system (Section S5).*

How are the chamber fill/empty times impacted by sample air getting between the PFA film and the lid? Could these factors impact lambda?

Response: *The fill/empty times are not impacted in terms of a measurable delay in volume exchange (e.g. stagnant pockets of air where the analytes slowly diffuse out and create hysteresis), as this would impact even our inert trace gases exchange for analytes like* CO_2 *and NO. There might be some impact on the more surface active gases, but all that is possible to quantify here is the net outcome, not the independent impacts of a sealed and unsealed system, because we do not have a version of the former to obtain the contrasting information. Since the net outcome is improvement across the board, the modified system with an unsealed PFA film performs better than bare acrylic. These factors therefore do not affect* λ *beyond the considerations around overall surface aging, which we have addressed with revisions to the associated comments preceding and following this one.*

Section 3.1.2: It would help to add callouts in this section, like where D and NO2 reactivity are discussed, to their respective details in the SI(S3 and S7).

Response: *Absolutely. Happy to do so.*

Modified:

L689-692:

"The determined surface **interaction** values (D; Table 1; **ES-2, Section S3**) demonstrate an expected greater impact of surfaces when no reactive gas is present in the headspace prior to filling, and a lesser effect during emptying **as the exposed** surface has equilibrated with the analyte, which is commonly referred to as passivation."

L708-710:

"For NO_2, specifically, we sought to quantify this as a function of modifying components of our chambers, as NO_2 is the most reactive gas in our suite **(Section S5)**. "

L630: Can you determine an **uncertainty for Lambda**?

Table 1 shows substantial differences in %D for the chamber empty vs. chamber fill times for NH3. Does %D change over the duration of the study period as the chamber gets dirty with usage? By the same reasoning, can or does lambda change over the duration of the study period (e.g., can or does Figure S11 change over time throughout the study period as the chambers are used and get dirty)?

Response: *Thank you for raising this point. We agree that λ is an empirically derived parameter and that both its uncertainty and potential evolution with surface conditions should be made explicit. That means our λ curves in the revised Figure S11 will change as the surface properties change. We now quantify the uncertainty in λ based on replicate fill-empty characterizations conducted under identical conditions, reporting one standard deviation (σ) for each gas. The λ values presented here therefore represent means with ±1σ for a pristine or lightly used chamber system.*

We additionally clarify in the text that surface aging or residue accumulation during extended field deployment may alter attenuation behavior, and that periodic re-characterization of λ is recommended to ensure reliable flux quantification. These clarifications are now included in the manuscript (see responses above) and the error is reported in the corresponding section of the Supporting Information. From the fluxes derived in the field, we note that these determinations have greater uncertainty than from our lab replicates and are already reported in Section 3.3.3.

Modification:

L187-196, Section S7.3, Surface interaction correction using the attenuation factor (λ):

"For NH_3, the fill-phase difference was 16.23, dividing the expected theoretical accumulation by this measured accumulation yields a λ_{fill} of 5.40, while the empty-phase difference was −16.44, with a λ_{empty} of 0.36. Unsurprisingly, NO_2 and HONO followed a similar trend as we also noted their surface interactions, with λ_{fill} values of 3.04 and 3.14 resulting from our characterizations, respectively, and λ_{empty} values near 0.40. **Uncertainties in λ were quantified from three replicate fill–empty characterizations under identical laboratory conditions, yielding one-sigma deviations of ±0.21 for NH_3, ±0.02 for NO_2, and ±0.02 for HONO. These values therefore represent attenuation behavior for a pristine or lightly used chamber system.**

From a physical and mathematical standpoint, attenuation reduces all concentration-dependent components of the flux (accumulation/depletion, dilution, and reaction) by the same factor. As a result, the attenuation factor λ scales the entire net-flux expression rather than only the accumulation term. **Because λ depends on surface condition, extended field use or residue accumulation may alter its value, and periodic re-characterization is recommended to maintain accurate flux estimates.**"

Figure 4: This is a nice figure. It's a bummer that there are no N2O or NH3 measurements for the samples with "none" and "AN" fertilizer application, as N2O and NH3 fluxes are predominant from the other treatments. Will a comparison of soils and treatments using this system be included in your forthcoming paper about the field study? That would also be an exciting addition to the literature. :)

Response: *We thank the Reviewer for their feedback and are hopeful that we may be able to do this in the future through collaboration with other researchers that have instruments to facilitate these measurements, or ourselves through successful instrumentation grants, as our access to the Picarro was limited in duration. A comparison of a fertilizer treatment with urea to unamended soil that includes N_2O and NH_3 is certainly in store for our future publication on the field study.*

Figure 5: The timescales in this figure could use some clarification, and this might be easily solved by simply adding some labels to each panel. These labels could simply say "after fertilization" for the NH3 time series and "before fertilization" for the NO and N2O timeseries. It is also unclear why the dates and times are not the same (e.g., 2 pm versus 5 am on 9/5/2022) for simultaneously measurements of NO and N2O during the "before fertilization" sampling. Is this because of differences in peak emission times as shown in Figure 3?

Response: *The dates and times shown in Figure 5 are intentionally not identical because the example cycles were selected to illustrate representative background flux behavior and term* *contributions for each gas, rather than simultaneous conditions. NH_3, NO, and N_2O exhibit distinct temporal dynamics and peak emission periods, and selecting a single common time window would not capture meaningful signal structure for all species. The purpose of Figure 5 is therefore methodological, demonstrating how rate, dilution, and reaction terms contribute under realistic conditions rather than enabling direct temporal comparison for all three gases simultaneously. We have clarified this in the figure caption and in the text associated with introducing Figure 5 to avoid potential confusion.*

Modification:

L1082-1089, Section 3.3.3:

"The **purpose of Figure 5 is methodological to demonstrate how rate, dilution, and reaction terms combine in the observed rates of concentration change during chamber cycles. The** selected data for NH_3 correspond to measurements taken after the fertilization event, while the selected NO and N_2O data segments are examples **for separate observations times which best demonstrated the contributions of all terms** prior to the fertilization event. **Taken together, these three separate examples for** the mathematical terms in E6 and E7 contributing to the net flux can be considered more easily – they are entirely ascribed to the rate term otherwise."

Figure 5 caption:

"Mixing ratios of N_2O (ppb), NO (ppb), and NH_3 (ppb) in the measurement (grey shading) and reference (unshaded) chambers from three consecutive cycles during the pilot field study. **Cycles are shown for representative, non-simultaneous periods to illustrate term contributions**. The NH_3 cycles correspond to measurements taken after the fertilization perturbation, while the NO and N_2O cycles are from the same period before fertilization. The dashed lines for the NO measurements indicate ±1 ppb (3σ noise), where the positive boundary represents the detection limit of the NOx analyzer."

Section 3.3.3: How would propagating an uncertainty in lambda impact the total uncertainties in the fluxes, especially for NH3? Since lambda is time dependent (e.g., Figure S11), can you comment on how a longer chamber sampling interval might impact the fluxes, again especially for NH3.

Response: *This is a great question. Our determined uncertainty is 4% for the 30 minute closure duration. Longer closures should reduce the uncertainty, as the second surface-driven time constant has longer to act wherein the surface sites are more extensively occupied by NH_3, which would decrease the uncertainty and the value of λ. That is, the mass transfer would be closer to* *unity. Shorter duration observations would lead to greater uncertainty as small changes in the surface interactions would have a greater impact on the assessed flux and the value of λ would increase. We have added this consideration as an example of the consequences for changing the chamber closure duration, along with a new panel in Figure S11, which were added in response to another Reviewer question. We show only the new text pertaining to this question, within the entirety of the new section of writing below.*

Modification:

L1120-1132, Section 3.3.3:

"For the 0.5 Hz measurement rate of the Picarro, it is clear from the accumulation and depletion of target gases in Figure 5, that a shorter observation period than 30 minutes could be used when high time resolution instrumentation across all target species is available. The benefit of this would be to reduce both the alteration of the composition of the chamber headspace and diverging physical conditions between the chamber and ambient environment; ultimately obtaining better flux estimates. However, for this pilot study, the 1-minute time resolution of the NO_x analyzer and the method for determining HONO by difference with an annular denuder every 5 minutes required the 30-minute interval. A shorter closure period could also have the drawback of worse flux detection limits when fluxes are small, and more variability due to a less robust regression of the accumulation or depletion rate. **For example, this would increase the value of λ for NH_3 and its relative error (4% for a clean system, Section S7.3) as well as other surface-interacting gases.**"

Sections S2 and S3: It seems that the instrument calibration methods for NH3 and HONO are missing from Section S2. It could be the case that the HONO and NH3 calibration sources used in Section S3 are also used to calibrate the analyzers and characterize instrument time responses. If that is the case, then I suggest reorganizing these sections to clarify. Along the same lines, section S2 should also describe how the analyzer response times are characterized. (Sorry if this is a repeat comment from above.)

***Response**: This is indeed a repeat from above and we have moved the calibration information from Section S3 to S2 as the Reviewer requested. Please see the changes implemented in the response above, if necessary.*

Section S7: It is helpful for readability if you can redefine parameters in the equations (like A, Q, F, c, R, X, t1, and t2, etc.) for the equations in the SI.

***Response:** We agree with the Reviewer on this change and have implemented it.*

Modification:

L5-10, Section S7:

“Where V is the volume of the chamber (m^3), *A* is the surface area (m^2) enclosed by the chamber and governing the gas flux; Qout is the volumetric flow rate of air exiting the chamber (m^3 s^{-1}; cm(t) and cr(t) are target gas concentrations within the measurement and reference chamber (mol m^{-3}), respectively; c_{in} and c_{out} represent their corresponding rates of change (mol m^{-3} s^{-1}); and Fnet is the resulting net gas flux per unit area (mol m^{-2} s^{-1}). The terms Rr denote the instantaneous chemical production or loss rate expressed in units of mol m^{-3} s^{-1} for consistency.”

Figure S9: Suggest adding the absorption cross section spectrum for NO2 to this figure for comparison. Can you estimate how modifying the chamber with the PFA film attached to the lid might impact loss by photolysis? Is there a transmission curve somewhere for this commercial material?

Response: *We agree with these suggestions. We have added the NO_2 absorption cross section to Figure S9 as requested. A wavelength-resolved transmission spectrum for the specific commercial PFA film used here is not available in the peer-reviewed literature. Manufacturer specifications indicate high UV–visible transparency (93%), consistent with the widespread use and rationale of PFA films in photochemical chamber applications. Unfortunately, we have not been able to track down a detailed description of this to plot, nor do we have the instrumentation to measure it. We note that the transmission reported in Pape et al. even states that the spectral transmission for their fluoropolymer film was obtained through a collaborative favour and was uninteresting enough that only an informal reference was made. Because the photolysis environment in our system is dominated by the polyacrylate lid and NO_2 photolysis contributes at most ~1% min^{-1} under clear-sky conditions, the absence of a detailed PFA transmission curve does not affect the interpretation of the results here.*

Modification:

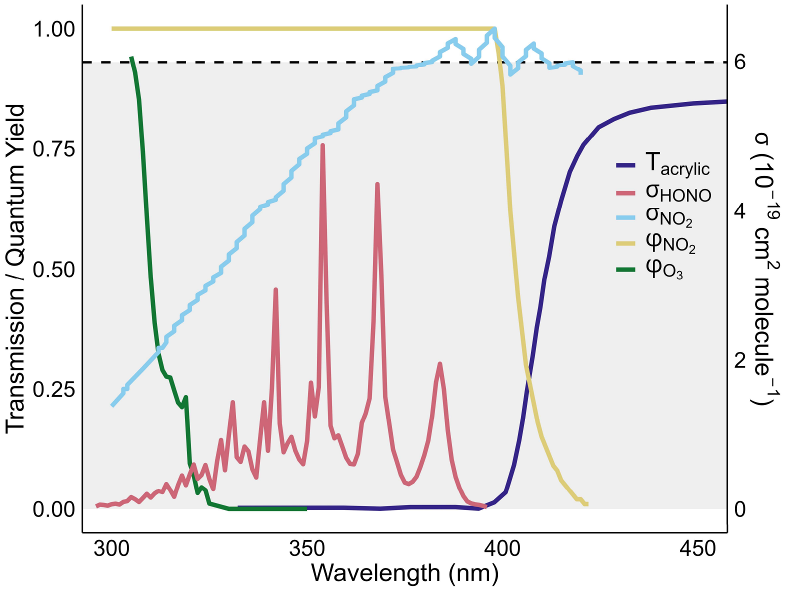


Figure S9. Transmission of light through the chamber and quantum yields for photolysis of O_3 and NO_2, **along with the absorption cross sections of NO_2 and HONO**, as a function of wavelength (Burkholder et al., 2020). **The shaded region denotes the manufacturer-specified minimum transmission (≥ 93%) for the PFA film**. Note the negligible overlap for photodissociation. The acrylic effectively blocks wavelengths below approximately 400 nm, meaning the photolysis rate of NO_2 is the only one impacted by a chamber constructed from this material.

Burkholder, J. B., Sander, S. P., Abbatt, J. P. D., Barker, J. R., Cappa, C., Crounse, J. D., Dibble, T. S., Huie, R. E., Kolb, C. E., Kurylo, M. J., Orkin, V. L., Percival, C. J., Wilmout, D. M, Wine, P. H. (2020). Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies - Evaluation Number 19. NASA JPL Publication 19-5. Tables 4C-1-2, 4C-1-3, and 4C-7-2. https://jpldataeval.jpl.nasa.gov/

Referee #2

Summary:

This manuscript presents the development and validation of a dual-dynamic chamber system enabling simultaneous flux measurements of multiple reactive nitrogen species alongside conventional greenhouse gases. The topic is interesting, given the increasing interest in quantifying Nr exchange processes and addressing their cascading environmental impacts. The study is ambitious and relevant: the integration of destructive analyzers, surface passivation strategies, and a dual-chamber configuration represents a potentially valuable contribution to the scientific community that deal with gas exchanges. The proof-of-concept laboratory and field applications, along with error characterization, support the method's applicability. Overall, the manuscript addresses a recognized gap in the simultaneous quantification of Nr species and GHG fluxes, and the results appear encouraging. The manuscript is well written and suitable for publication in AMT, and I recommend its acceptance. Nevertheless, I have a few minor suggestions regarding structure and clarity in specific sections, as well as some questions that may lead to further elaboration in the text.

Response: *We thank the Reviewer for their positive view on this work and the helpful suggestions below. Some of their comments conflict with that of the other Reviewer and we have done our best to navigate the opposing suggestions to occupy a fruitful, yet concise, middle ground.*

General Comments

The manuscript is rich in technical details and provides valuable information that can support reproducibility by other research groups, which is a key strength of the study. Nevertheless, I have several general observations related to structure and readability, some of which are expanded in the specific comments in the next section. For now, the general suggestions is the following:

In its current form, the **abstract appears excessively long**. Even for a complex methodological study, an abstract should provide a concise synthesis focused on essential elements: state of the art, research gap, objectives or hypotheses, methodological approach, key results, and main conclusions. Many of the finer details presented there would be better placed only in the main text.

Response: *We agree and this has been completely re-written to shorten the length and focus on the core findings of our work.*

Modification:

About 17 lines of text have been cut to remove ancillary information, which is more than half of a page.

A similar issue arises with **the introduction, which is pretty long and demanding to read.** Condensing this section could enhance accessibility, particularly for readers primarily interested in process-oriented assessments rather than methodological development. Given that such readers may represent a substantial portion of the intended audience, a more streamlined introduction could improve engagement without sacrificing scientific relevance.

Response: *We agree and have edited the entire introduction to improve its readability, aiming to better focus on the main points of this work. Since the main target audience for this journal are those interested in 'measurement techniques', we have retained the deep review of methodologies and knowledge gaps pertinent to* N_r *flux measurements.*

Modification:

We have removed over 20 lines of material from the introduction and streamlined its contents, nearly equivalent to 1 page.

Additionally, where feasible, I encourage **updating some of the citations**, as many references are 15–20 years old and more recent literature could strengthen the framing.

Response: *We appreciate where the Reviewer is coming from with this comment and have implemented their suggestions below, as appropriate. However, we must point out that we have cited more than 60 papers that are less than 10 years old and respectfully disagree with their view that there is a strong impetus to update the citations in a more extensive manner.*

The **results section is also extensive**. While this reflects the dense amount of findings, a more concise presentation focused on the key messages would improve clarity. The scientific content is strong and insightful, but at times becomes redundant or overly verbose. A tighter structure could help highlight the main contributions more effectively.

Response/Modification: *The overall length of the manuscript is now nearly 10 pages shorter, with much repetition or superfluous material removed throughout, including the results and discussion. Roughly 2-3 pages of material have been relocated to the SI to focus the manuscript more directly on* N_r *species and the hardware critical to our field deployment.*

In contrast, **the conclusions appear relatively short compared to the rest of the manuscript**. Expanding this section to further emphasize applicability, remaining uncertainties, and open research questions would reinforce the overall impact of the work and guide future studies more clearly.

Response: *In response to the other Reviewer, and the suggestions below, our conclusions are now expanded to address several topics.*

Specific comments:

L122: Suggesting to add a couple more up to date references:

Chiaravalloti et al., 2023: https://doi.org/10.3389/fclim.2023.1203043

Anthony & Silver, 2024: https://doi.org/10.1007/s10533-023-01095-y

Manco et al., 2025: https://doi.org/10.3390/horticulturae11060708

Response: *We thank the Reviewer for suggesting some additional references to connect with more recent reports and have been implemented them, where appropriate. These are focused on greenhouse gases, however, and not reactive nitrogen species which are the focus of this work. We note that for the reactive analyte suite, that we have cited over 60 relevant publications from the past 10 years to build the context for this work. Where older works are being drawn upon, this is because the necessary instrumentation to modernize some of the pioneering approaches to chamber-based fluxes have only recently been developed, so instead of a continuity of literature the state of the science has been more of a leap in capability across more than ten years. We realize this is not the case for greenhouse gas observations, like* N_2O*. Yet this is not actually a reactive nitrogenous gas, as its ultimate fate is photolytic destruction in and above the stratosphere. We have allowed it some prominence in this work, given its longstanding study and linkages to agricultural soils which we use for our proof-of-concept measurements, as well as for completeness in our measurement suite.*

Modification:

Lines 126-128:

"Chambers are limited to small plots, making them suitable to study the effect of different fertilizer treatments (Anthony & Silver, 2024; Chiaravalloti et al., 2023; Manco et al., 2025; Tang et al., 2020)."

L131-144: I would suggest reorganizing the presentation of reaction schemes. Similar to the equations used later in the manuscript, each reaction could be introduced within the relevant section of the text, framed in a small boxed or separated layout, and assigned a numbered identifier in parentheses for subsequent citation. For example:

"…at night, if sufficient O_3 is present to fully titrate NO"

$NO + O_3 \rightarrow NO_2 + O_2$ (R1)

$NO_2 + O_3 \rightarrow NO_3 + O_2$ (R2)

This approach is preferable to listing all reactions together only once in the early part of the Materials and Methods, as it improves readability and allows the reader to refer to each reaction when it is conceptually needed.

Response: *The location for these reactions is currently in its most relevant location and presented consistently with such reactions for the atmospheric chemistry community. Having the reactions grouped together in one location makes navigating to them, in our opinion, easier than listing at each relevant point or first mention in the methodology or results and discussion. We consider several of these reactions at multiple points, and some of them are only relevant for broader atmospheric context, which would then disjoin the chemical framework. As a result, we have opted to retain the presentation of our reactions as-is.*

L158-159: Also for this part I suggest more up to date references, like: Pugliese et al., 2023 https://doi.org/10.1038/s41467-023-40661-8

Response: *We appreciate the Reviewer's suggestion. The most up to date references are added to this section and the paragraph has been modified accordingly.*

Modification:

L163-168:

"The dynamic chamber **flux** method has measured challenging gases like biogenic volatile organic compounds, such as monoterpenes and isoprene, from vegetation and farmland (Kolari et al., 2012; Mochizuki et al., 2018; **Pugliese et al., 2023**), NH_3 volatilization from cattle manure (**Becciolini et al., 2024**) , N_2O and NO_x from turfgrass (Maggiotto et al., 2000), and NO_x fluxes from grasslands (Pape et al., 2009; Plake et al., 2015)."

L177-179: As suggested before, there are a plenty of more up date publications to refer to, about meaurements of GHG and Nr with soil chambers in relation to fertilization. Regarding GHG, I have listed some of them before.

Response: *We appreciate Reviewer's suggestion. We have added a few more recent references related to subsets of N_r measured following fertilizer applications.*

Modification:

L186-190:

"This N_r exchange in agricultural regions from excessive nitrogen inputs are prime targets for chamber methodologies, as they amplify emissions of all N_r species **(Degaspari et al., 2020; Huber et al., 2020; Manco et al., 2025)**."

L275-279: I suggest to explain in details the gas analyzer equipments only in the Section 2.1.3. There is no utility to list them at the end of this already long section.

Response: *We agree with this reduction in redundant information and thank the Reviewer for the suggestion. We now simply refer the reader to Section 2.1.3 for details on the instrumentation.*

Modification:

L317-318:

"All instrument and operational details are provided in Section 2.1.3."

Section 2.7: I am referring with this larger comment to this section, but these aspects appear also in other sections of the manuscript. Indeed, like in the general comment, I suggest the author to try to optimize and gather all the discussion about this in one section into the discussion.

Dealing with the specific observation...

A further point that may require clarification concerns the attenuation factor used to account for surface interactions, particularly for highly reactive species such as NH_3. The manuscript discusses chamber wall effects, but it is not clear whether the authors considered potential losses along the sampling lines. Reactive gases like NH_3 may interact significantly not only with chamber surfaces but also with tubing, connectors, internal multiplexer components, and the analyzer inlet, and these losses typically scale with tubing length and residence time.

For example, field chamber systems—such as those deployed for multi-site measurements or spatially distributed installations—may involve sampling lines up to 30–35 m in length. In such configurations, tube material, conditioning, and line heating are commonly used mitigation strategies (as applied also in VOC measurements) to reduce wall adsorption under low flow rates. It would therefore be useful to know:

- What tubing materials were used in this system?
- What were the actual sampling line lengths, and were they varied and characterized?
- Were line losses quantified in relation to the tube length, and if so, how were they incorporated in the attenuation correction?
- Did the authors consider or test heating of the sampling lines to minimize adsorption effects, particularly for NH_3?

Providing this information would strengthen confidence in the attenuation treatment and in the transferability of the system to field deployments where sampling geometries differ from the laboratory setup.

Response: *With a systematic investigation progressing from an assessment of materials through practical field use, the discussion needs to remain organized in its current format. The focus of this journal is the measurement methodology, so our sections are structured based on the methodological progression, not gas-by-gas. We have thoroughly addressed all of the points here in response to the Reviewer above, particularly for* NH_3*, where we are acutely aware of the surface interactions noted here and below. Based on our discussions with the Eosense team, we avoided the use of heating tapes on the tubing at this time to prevent subsequent water condensation in cooler downstream valves and lines that could be quickly damaged, particularly during hot/humid summer conditions present in Southern Ontario. It is certainly something worth considering in the future. We have added commentary on this in the fieldwork Section 3.3.3 where our* NH_3 *discussion is expanded, and in the Conclusions.*

Similarly, their data transfer cables for the chambers are 15 m in length, so we simply characterized gas transfer lines with this maximum length. Based on our literature review and discussion, we felt that this consideration is implicit, but see now that our oversight in specifying this information would make it ambiguous. We have made revisions throughout as part of our full manuscript edit to keep this as clear as possible, noting a few specific instances below.

To briefly summarize with respect to system components used: All tubing, connectors, and instrument components were included in the assessment of surface interactions and our lab experiment flow rates were matched to those used in the field to provide transferability between the characterization and the application.

We have clarified this at the outset of the methodology section and the surface considerations already included in detail in the results associated with this gas should now have more implicit impacts, as well as in the SI. We now clearly state was that the system characterized was the same *as what was deployed in the lab and field, along with the tubing material and length. The few exceptions to this are now also more clearly noted.*

Modification:

Throughout:

In our full revision, several instances of emphasis on our use of the standard 15 m PFA sampling lines have been implemented to improve clarity and comparability between experiments.

L257-259, Section 2.1.1:

"**The RC acts as a negative control for physical interactions and/or associated chemistry of reactive gases on chamber and gas transfer line surfaces.**"

L408-411, Section 2.3:

"It was expected that N_r gases **would interact and/or react** on chamber surfaces and **15 m of standard** sampling tubing that would differ between the unmodified and modified variants."

L433-436, Section 2.3.1:

"**All assessments herein matched: the standard configuration of the chambers with all fittings, 15 m of ¼" O.D. PFA gas transfer tubing, flow rates, valves and gas transfer lines to instrumentation, with line/fitting/valve/instrumentation surfaces included.**"

L698-706, Section 3.1.2, Discussion:

"The surface interactions for these gases are minimized in the modified chambers to facilitate more time-efficient measurements of surface exchange. However, they necessitate the use of the λ term when deployed in the measurement-reference configuration for those N_r species which experience partial transmission, such as NH_3. The λ term is required to obtain accurate values, as the enclosed flux measurement surface should be perturbed for the least amount of time possible when making field measurements, and the chambers cannot be closed for several hours to allow surface-active gases to passivate the lines. **One potential option to improve the system performance further for NH_3 could be to heat the gas transfer lines between the chambers and gas analyzers.**"

L1261-1267, Conclusions:

"The time constants for the transfer of GHGs were not different from those of a theoretically inert gas and showed no change from the modifications. Improved transmission for the reactive and surface-active N_r species NO_2, HONO, and NH_3 targeted here ranged from 0.8 to 2.6 minutes. **Further improvement for NH_3 might be obtained by integration of heated gas transfer lines between the chambers and gas analyzers.** Similarly, a commercial chamber multiplexing unit with stainless steel valves and fittings replaced with PTFE and PFA, respectively, resulted in a 9–27% reduction in surface losses of N_r compounds."

L131-136: A clarification may be needed regarding the derivation and implementation of the attenuation factor (λ). The current definition — "the ratio of the theoretical concentration signal to the measured signal over the chamber closure period" — raises several questions. Specifically, it is not clear what is meant by "theoretical concentration":

- Is this inferred from a mass-balance model, expected accumulation kinetics, or an external reference concentration?
- Does it rely on empirical baseline values, tabulated concentrations, or ambient background levels?
- How sensitive is λ to assumptions about these theoretical inputs?

Response: *We are happy to clarify here and in the main manuscript. The theoretical concentration would be that of an inert gas that does not interact with the chamber surfaces. We have now been clear on this definition in the methods and then again at this location in the discussion. As part of our full manuscript editing, we have found several other instances to clarify this as well and have done so.*

The main assumption here is that the empirically characterized value under controlled lab conditions applies under all field conditions, which is reasonable, but subject to both passivation and aging effects in terms of error. Passivation would mean that the attenuation is less severe than under the controlled characterization, while aging effects would lead to the opposite effect. In response to the other Reviewer, we have tried to provide a 'sneak peak' at the magnitude of this issue from a second 6-week study where our chambers were operated continuously and exposed to much more challenging environmental conditions than in our pilot study. From this, we found that the overall error corrected for by using our empirical λ value (i.e. a systematic error of a factor of more than 5) is greater than the resulting uncertainty in its value when accounting for the dynamic nature of the surface interactions. For the lab and fieldwork shown in this manuscript, changes in surface performance were not different from that described for our system with newly installed PFA films. As noted with the revisions for the other Reviewer, we have happily added in cautionary guidance to our readers on the necessity of characterizing the value of λ in situ with the reference chamber as frequently as possible during extended field use at several points in the manuscript (please see above, as we realize this response is already very long).

Because λ is a key component in correcting surface interaction artefacts for reactive gases, the conceptual basis and calculation procedure would benefit from clearer explanation. I would recommend introducing a concise but explicit description of how λ is computed in the Materials and Methods section rather than within the Results. Additional procedural detail — including underlying assumptions, modelling basis, and any validation performed — could be provided in the Supplementary Information to ensure transparency and reproducibility.

Response: *Seeing as this is a misunderstanding stemming largely from our use of the word 'theoretical' without re-definition at this location, we believe that the issue here is solved by revision for clarity. We are comparing the transmission of an inert gas relative to our experimental fill-empty observations for a surface interacting one, and the terminology is internally consistent with our use and description of a 'theoretical' gas in Figure 2. Overall, λ is an empirically measured quantity from our lab fill/empty experiments with* NH_3 *and the only assumption we make is that the surface effects are similar in the field.*

To obtain the discrete value of λ from our empirical measurements, we take the integral of the inert-to-interactive ratio of gases from both fill and empty cycles in our experiments to capture the overall systematic difference for a sticky gas relative to an inert one. Since the interactions are non-linear for a sticky gas, the λ value presented in this work applies to our explicit 30 min measurement period – a fact which we have clarified (see below for an example, and responses for the other Reviewer above for more). Figure S11 shows that this system is non-linear, and so the value of λ changes with the chamber closure duration, which is another point we have clarified in our Section 3.3.3 discussion on the field use of the system for the other Reviewer.

Since the determination of λ required experiments, we feel that its placement in the results of this work is warranted. We have made a few changes to clarify the linkages between the methods and the results. After careful review, the derivation and methodology of this is too long to place in the main manuscript and the material therefore needs to remain in the SI since oth Reviewers have asked us to shorten the contents of this paper. As λ is a key requirement mostly for NH_3*, and even then only for our fieldwork, we feel this is a reasonable compromise and it is extensively presented in the Supporting Information. We hope that the following clarifications, description in the methodology, and expanded details in the SI are sufficient to resolve this issue for the Reviewer.*

Modification:

Lines 479-482, Methods, Section 2.3.2:

"The ratio of the transferred gas amount to the nominal was used to identify impacts of surface interactions on quantitative transmission to downstream gas analyzers. Further details are presented in **Sections 2.7, and S4**."

Lines 613-622, Methods, Section 2.6:

"The dimensionless attenuation factor λ is required to correct for interactions of reactive gases with surfaces. Such surface interactions, which are particularly strong for gases like NH_3, significantly reduce the measured rate of concentration change within the closed chamber (Figure 4). Thus, λ is derived as the ratio between a theoretical unattenuated gas **(i.e. an inert GHG like N_2O)** and the target gas concentration from controlled deliveries integrated over the chamber closure interval as derived in Section S7. **This term has the surface effects from chambers, gas transfer lines, and analyzers embedded by definition and must be determined empirically for any altered configuration.** The attenuation correction removes bias from **surface-induced** artifacts in flux estimates, so that more accurate soil–atmosphere exchange is reported."

Lines 1119-1123, Section 3.3.3:

"A shorter closure period could also have the drawback of worse flux detection limits when fluxes are small, and more variability due to a less robust regression of the accumulation or depletion rate. For example, this would increase the value of λ for NH_3 and its relative error (4% for a clean system, Section S7.3) as well as other surface-interacting gases."

Lines 64-69, SI, Section S7.1:

"Last, we introduce a flux **attenuation** factor (λ; ES12) to correct for partial transmission of a targeted reactive gas due to adsorption to chamber walls and gas handling lines during a measurement cycle (t_1-t_2). This factor needs to be determined empirically through calibration experiments, like those presented in Figure 2, **where the loss of the surface-active gas is quantified relative to the transmission of an inert gas during both filling and emptying processes.**"

Lines 159-165, SI, Section S7.3:

"The attenuation factor is derived from our controlled delivery experiments that simulated two sequential measurement scenarios: a filling phase, where gas is introduced and accumulates within the chamber, and an emptying phase, where the chamber is flushed and the gas signal declines (Figure 4). **For an ideal gas** without wall interactions, the integrated difference between theoretical and observed concentrations within a single chamber should approach zero, and λ would be approximately one. However, as shown in Figure S11, all three gases exhibited surface interactions, with NH_3 showing the largest deviation from **an inert gas model.**"

L1044-1046, Figure 6: "Error bars are calculated using the mean value of the corresponding terms from three reference chambers plus their standard deviation".

I did not understand properly why the error bars were calculated using mean and SD of the reference chambers.

Maybe it is very simple, but it is not clear to me at this point.

Response: *The Reviewer should be confused and we apologize for creating this issue. This is an overt error on our part during the internal revisions process amongst co-authors. The sentence was edited incorrectly, and we have revised it now to fix the caption description for accuracy and present the propagation of error correctly. It was also presented incorrectly in the main text associated with this figure. It is derived for each term contributing to the overall flux using the mean and standard deviation from three consecutive chamber cycles, inclusive of the reference chamber corrections.*

Modification:

Line 1134-1139, Section 3.3.3:

"We consider these across **a consecutive triplicate of flux determinations** from the pilot field deployment, to provide meaningful examples. The uncertainty in each term is estimated from the variance between the triplicate of consecutive **measurement and reference chamber observations, through the measured slopes (i.e. using E6 or E7)** and assumes that ambient atmospheric composition did not change substantially during this error derivation period."

Figure 6, Caption:

"Figure 6. Contributions of different terms (rate, dilution, and reaction) to the net flux of NO, NH_3, and N_2O across three consecutive cycles (nmol m^{-2} s^{-1}). The rate represents the change in concentration measured over time, the dilution represents the integrated loss to dilution, and the reaction represents the contribution of known reactions happening inside the chamber. Error bars are calculated using **the standard deviation about the mean** of the corresponding terms **from three consecutive chamber cycles**. For visual clarity, the attenuation correction ($\lambda = 5.40$) for NH_3 is not applied in this figure, as it constitutes a linear scaling factor across all NH_3 bars (Section S7.3)."

L1066-1070: I believe it would be useful to cite Manco et al. (2025; https://doi.org/10.3390/horticulturae11060708) to provide a more complete context. Under granular urea fertilization, that study reported hot-moment emissions approaching ~3 nmol m^{-2} s^{-1}, which appears relevant for comparison with the flux magnitudes discussed here.

Response: *We have reviewed the mentioned manuscript and include it in our literature survey as part of the static chamber N_2O flux comparison. The reported hot moment fluxes of N_2O are 0.5 nmol m^{-2} s^{-1}, however, which is well within the observations we report in our example here. The 3 nmol m^{-2} s^{-1} seems to be from the CO_2 fluxes measured.*

Modification:

Lines 1186-1190:

"The N_2O fluxes observed here are consistent with those reported for European arable soils using both dynamic and static chambers, where event-driven N_2O peaks after fertilization commonly range between 0.2 and 2.4 nmol m^{-2} s^{-1}, and background periods can be as low as 0.08 nmol m^{-2} s^{-1} (Kong et al., 2025, Murphy et al., 2022, Maier et al., 2024, **Manco et al., 2025**)."