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

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Abstract

Reactive nitrogen compounds (NO, NO_2, HONO, NH_3 and others; N_r) play important roles in atmospheric processes, and their cascading impacts throughout the Earth system have adverse effects on both the environment and human health. The fluxes of these gases at the surface-atmosphere interface have been studied in isolation or in smaller subsets by micrometeorological techniques or chambers, but simultaneous observations of all N_r species alongside standard greenhouse gases (GHGs) as a function of time have not been reported. Here, a dual-dynamic chamber system was developed for N_r by modifying a commercially available system for GHG fluxes for use with destructive analyzers and to account for chemical changes. The resulting platform makes the measurement of N_r and, by extension other reactive gases, more widely accessible to the scientific community, as custom chambers do not need to be fabricated.

System modifications to passivate surfaces were implemented, so that N_r gases like NO_2 could be effectively transferred to standard gas analyzers, with an initial 36% loss due to transformations ultimately minimized below analyzer detection limits (~10%) under relevant atmospheric conditions. The modified 72 L chamber did not see a change in the baseline response times for GHGs or NO at a flow rate of 2 L min^{-1}. They retained the same values as an ideal non-reactive

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trace gas (τ = 37-39 min versus 36 min. The modifications improved the transfer time constants of NO_2, HONO, and NH_3 by up to 2 min, but substantial surface interactions for NH_3 remain. In all cases, a surface interaction term needs to be characterized for these gases to obtain accurate fluxes. Losses of NO_2 and O_3 by known gas phase reactions, or from deposition and reaction on pristine and aged chamber surfaces, were characterized across a range of environmentally relevant relative humidities (RH) and mixing ratios. The final dual-chamber system configuration includes a measurement and reference chamber, which are necessary to implement the corrections for surface effects and chemical transformations when accurately quantifying dynamic fluxes via a mass balance framework.

Proof-of-concept measurements of N_r fluxes from agricultural soil samples under controlled lab conditions as a function of soil water content were able to quantify emissions of NO, NO_2, HONO, NH_3, and N_2O simultaneously, when subject to fertilization experiments using urea, ammonium carbonate and bicarbonate, and ammonium nitrate. Unfertilized replicate agricultural soil samples showed variability in NO_2 and HONO emissions when prepared with minimal disturbance to the soil structure, with values consistent with those reported by in-situ field measurements. These oppose maximum potential fluxes characterized in prior lab soil manipulations, particularly for HONO relative to NO. Last, fluxes were quantified with destructive gas analyzers in the field with the dual-chamber system on an in-use agricultural soil and included a urea-based fertilizer perturbation to stimulate microbial and chemical transformation and transfer N_r to the atmosphere. The resulting fluxes observed show good agreement with prior reports based on other flux techniques. The mass balance terms within the dual-chamber approach are fully inspected from the pilot deployment in the field, along with an error analysis, to aid in the uptake of this approach by the community.

1 Introduction

The nitrogen (N) cycle is a crucial biogeochemical cycle on Earth, essential for sustaining life through the production of nucleic acids, proteins, and other vital biomolecules (Lehnert et al., 2021). Although the carbon cycle receives the most attention due to looming climatic crises caused

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by greenhouse gases (GHGs) like carbon dioxide (CO_2) and methane (CH_4), the N cycle is closely intertwined with the carbon cycle (Schlesinger, 2020). At the interface of these cycles and the Earth's surface, reactive nitrogen (N_r) species exchanged between ecosystems and the atmosphere have become an area of emerging interest (Lehnert et al., 2021; Wu et al., 2020). Within the atmosphere, N_r species such as nitric oxide (NO) and nitrogen dioxide (NO_2) – collectively referred to as NO_x – ammonia (NH_3), and nitrous acid (HONO) can each be mediated in part through surface-atmosphere exchange, influencing local air or water quality, ecosystem processes, and biodiversity (Lehnert et al., 2021; Richardson et al., 2023; Wu et al., 2020). Meanwhile, the non-reactive nitrous oxide (N_2O) has climate impacts due to its long atmospheric lifetime (~120 years) and potent greenhouse effect (IPCC, 2023).

Reactive nitrogen compounds (NO, NO_2, HONO, and NH_3; N_r) play an important role in atmospheric processes, contributing to the formation of pollutants like ozone (O_3) and secondary organic aerosols (SOA). The exchange of N_r between the Earth's surface and the atmosphere involves numerous production and loss processes driven by both natural and human activities. Reactive nitrogen species are removed from the atmosphere through wet and dry deposition, and their abundance depends on the net outcome relative to N_r emissions (Delaria & Cohen, 2023). At the land surface, N_r is released into the atmosphere by microbial nitrogen cycling, agricultural activities, wildfires, or fossil fuel combustion (Benedict et al., 2017; Mosier, 2008; Yang et al., 2024). Despite the wealth of knowledge on the environmental importance of N_r, studying N_r at the surface-atmosphere interface with high time resolution and chemical speciation remains a challenge due to its high spatial and temporal variability driven by factors like climate, vegetation cover, and soil/surface properties (Ludwig et al., 2001). For example, recent studies have demonstrated that HONO production at the ground surface plays a major role in the unexplained daytime HONO source and its impact on daytime OH, with vertically resolved measurements confirming that the surface remains a dominant source at all times of day (VandenBoer et al., 2013, 2015; Young et al., 2012). Such observations pose a challenge in studying N_r because suitable equipment for high time resolution atmospheric observations is expensive, limiting the concurrent study of the interplay between emission and deposition for many N_r species to one or a few species at a time. As a result, no systems are currently accessible enough to the scientific

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community that they may be deployed across widely different global landscapes, but particularly soils.

Soils play a pivotal role in mediating N_r emissions due to their dual function as both a source and a sink of nitrogenous species. Soil-atmosphere exchange of N_r is thought to be governed by microbial processes such as nitrification and denitrification, with soil factors like pH, moisture, organic matter, and nitrogen availability playing a crucial role in regulating N_r emission (Mosier, 2008; Purchase et al., 2023; Stepniewski et al., 2015). These microbial processes have been demonstrated to drive the formation and release of some N_r species (e.g., NO, NH_3 and N_2O) in addition to assertions that they can support the production and release of HONO via partitioning (Butterbach-Bahl & Dannenmann, 2011; Kool et al., 2010; Mushinski et al., 2019; Oswald et al., 2013; Su et al., 2011). Understanding the exchange of these gases is essential for unravelling the complex interactions between the nitrogen and carbon cycles and their broader environmental impacts from an unprecedented imbalance in the global nitrogen cycle (Richardson et al., 2023). Given the importance of N_r in atmospheric chemistry and its influence on ecosystem processes, it is essential to understand the mechanisms driving its exchange (Fowler et al., 2013). To date, comprehensive exchange systems for studying the full suite of N_r have not been reported.

To quantify N_r exchange for a few explicit species near the ground surface, various flux measurement techniques have been employed, yielding insights into their magnitude and identifying some driving factors. Quantifying fluxes of atmospheric gases has been most effectively applied to GHGs at the surface-atmosphere interface. Traditional measurement methods, such as eddy covariance (EC), relaxed eddy accumulation (REA), and aerodynamic gradient (AG) methods, have been extensively used for ecosystem-scale, continuous flux monitoring, including targeted assessment of most N_r species (e.g., (Bao et al., 2022; Geddes & Murphy, 2014; Kamp et al., 2020; Laufs et al., 2017; Min et al., 2014; Moravek et al., 2014, 2019; Ren et al., 2011; Von Der Heyden et al., 2022; Wang et al., 2022; Wolff et al., 2010). These micrometeorological techniques measure concentrations, concentration gradients, and/or turbulence to estimate fluxes across interfaces applicable to ecosystem-scale processes. When operated continuously, they offer long-term insight without disrupting the natural system. Chamber methods have some advantages compared to micrometeorological techniques, as they are relatively inexpensive, easy to deploy, and require minimal prior meteorological training and

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expertise (Tang et al., 2020). Chambers are limited to small plots, e.g. making them suitable to study the effect of different fertilizer treatments (Tang et al., 2020). The chamber method is a widely used technique for measuring GHG fluxes, especially for N_2O. However, challenges remain in addressing potential biases introduced by chemical transformations occurring within the chamber and interactions with the chamber surfaces, particularly for N_r species (i.e., NO_2, HONO, NH_3).

Chemical transformations can occur on chamber surfaces or between the point of emission and measurement. Surface interactions such as adsorption, desorption, and heterogeneous reactions can alter the apparent concentration of several N_r species. For example, NO in a chamber could react in the gas phase with O_3 to form NO_2 during the day and NO_3 at night if sufficient O_3 is present to fully titrate NO (R1, R2). Heterogeneous reaction of gas-phase NO_2 on surfaces under humid conditions also produces nitric acid (HNO_3) and HONO (R3) (Kleffmann et al., 2005; Ramazan et al., 2004; VandenBoer et al., 2015). The formed HONO can undergo multiphase processes in the chamber or on enclosed surfaces by partitioning into water according to its Henry's Law constant and then dissociating into nitrite (NO_2^-) and the hydronium ion (H_3O^+) according to its acid dissociation equilibrium constant and the pH (R4, R5) (He et al., 2006; Ren et al., 2020). Nitrous acid could also photolyze, yielding NO and an OH radical (R6) (Spataro & Ianniello, 2014).

$$NO + O_3 \rightarrow NO_2 + O_2 \quad \text{(R1)}$$

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \quad \text{(R2)}$$

$$2NO_{2\,(g)} + H_2O_{(ads)} \rightarrow HONO_{(g)} + HNO_{3\,(ads)} \quad \text{(R3)}$$

$$HONO_{(g)} \leftrightarrow HONO_{(aq)} \quad \text{(R4)}$$

$$HONO_{(aq)} + H_2O_{(l)} \rightleftharpoons NO_2^-{}_{(aq)} + H_3O^+{}_{(aq)} \quad \text{(R5)}$$

$$HONO + h\nu \rightarrow NO + OH \quad \text{(R6)}$$

These processes in/on the chamber can introduce uncertainty in flux measurements. Characterizing and accounting for chemistry and surface effects in chamber-based methods are necessary to obtain accurate flux measurements of N_r species with a chamber-based system. While static chamber systems typically determine the flux from the change in concentration after closing the chamber

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cover, traditional dynamic chamber systems use a controlled flow of ambient air through the headspace and retrieve the flux from the concentration difference at the chamber inlet and outlet. With minor modifications, these chambers have previously been applied to agricultural soils and natural ecosystems, demonstrating their utility for measuring emissions of gases such as N_2O and NO_x (Maggiotto et al., 2000; Pape et al., 2009). Their ability to create standardized and reproducible conditions makes them particularly advantageous for studying the driving mechanisms behind gas exchange, yet their application to the full suite of relevant N_r species for surface-atmosphere exchange remains unestablished.

The dynamic chamber method has been reported for measurements of the exchange fluxes of challenging gases like biogenic volatile organic compounds (BVOCs, such as monoterpenes and isoprene) from vegetation and farmland (Kolari et al., 2012; Mochizuki et al., 2018), 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, Sörgel, et al., 2015). Scharko et al. (2015) used sealed chambers and Tang et al. (2019), using dynamic chambers, were amongst the first to highlight the potential for both HONO and NO_x fluxes from agricultural soils as hotspots impacting atmospheric chemistry, which has been implemented in atmospheric models (Ha et al., 2023; Tian et al., 2024).

The complexity of nitrite (NO_2^-) chemical and biological production and loss in soils, coupled with soil properties facilitating gas exchange of HONO, has led to intense interest and debate around discerning the fundamental controls on its surface-atmosphere exchange (R4, R5) (Barney & Finlayson-Pitts, 2000; Huang et al., 2002; Kamboures et al., 2008; Meusel et al., 2018; Mushinski et al., 2019; Purchase et al., 2023; Song et al., 2023; Sörgel et al., 2015; Wang et al., 2021). The same is true for direct emissions of NO_2 from soils, where evidence remains limited (Huber et al., 2024; Zörner et al., 2016). Only a handful of field studies have directly measured soil NO_2 measurements, making it challenging to infer how much NO_2 might be emitted from soils. .Gong et al. (2025) estimates that fertilizer-induced soil NO_x emissions contribute 0.84–2.2 Tg N yr^{-1} globally, with uncertainties partly due to the lack of NO_2 measurements. Their modelling indicates that this underrepresentation likely leads to underestimation of summertime ozone enhancements (0.3–3.3 ppbv) in agricultural hotspot regions. This N_r exchange is intricately linked to agricultural practices, as excessive nitrogen inputs (e.g., fertilizers) amplify emissions of N_r species, namely

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NO_x, N_2O, HONO, and NH_3 from the impacted soils (Degaspari et al., 2020). These issues highlight the need for more direct soil NO_2 and HONO measurements, as well as simultaneous constraints on the entire N_r suite being exchanged from soils.

Automated dynamic chambers deployed in situ for field observations would provide a platform for capturing (and manipulating) 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 (Aneja et al., 2006). 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.

Here, we modify commercial dynamic chambers originally designed for GHG flux measurements to make them suitable for quantifying the most prevalent N_r gas exchange fluxes at surface-atmosphere interfaces. First, we implement surface and hardware modifications to adapt the commercial chambers to minimize gas adsorption and transformations. 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. Flux bias minimization through a mass balance approach during the pilot study in a real agricultural field is demonstrated for several N_r gases. This community-accessible approach addresses key needs in allowing more researchers to measure N_r exchange at the surface-atmosphere interface, with the capacity to monitor fluxes of all species simultaneously with at least hourly time resolution.

2. Materials and methods

2.1 Dynamic Chambers for Field Fluxes

2.1.1 Description of the custom-modified dual-dynamic chamber system for flux measurement

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The dynamic chamber system is composed of two identical commercially available chambers (eosAC-LT Eosense, Dartmouth, NS). These are modified and coupled to programmable valves that control the delivery of sample gases to a suite of instrumentation (Figure 1) to perform reactive gas flux measurements.

The dynamic chambers, constructed out of transparent polyacrylate walls and lids, have an internal volume of 0.072 m^3 and can enclose a surface area of 0.21 m^2. When used on soil surfaces, the chambers are secured with embedded soil collars using custom-made polytetrafluorethylene (PTFE) rings (Figure S1) and can be similarly affixed to impervious surfaces. A built-in fan ensures uniform distribution of gases inside the chamber. Ambient air temperature is measured inside the chamber from the fan arm, whereas pressure sensors are embedded in the control box outside the chamber. Each chamber has two auxiliary ports, one internally and the other externally, capable of collecting measurements of environmental properties such as relative humidity (RH), photosynthetically active radiation (PAR), soil temperature, and soil volumetric water content (VWC).

For a N_r sampling approach, one of the two chambers is used as the measurement (MC) to enclose an experimental surface while the second chamber acts as a reference (RC) by being sealed at the bottom with a film of 0.002" perfluoroalkoxy alkane (PFA; McMasterr-Carr®, PN: 84955K24). The inert PFA film is held in place between the chamber collar and our custom-made PTFE rings (Figure S1). This modification provides a negative control observation for physical interactions on apparatus surfaces and associated chemistry when sampling reactive gases. The use of the RC, therefore, is to facilitate the correction of surface-mediated effects, reactions, and reduction of bias when determining quantitative flux values.

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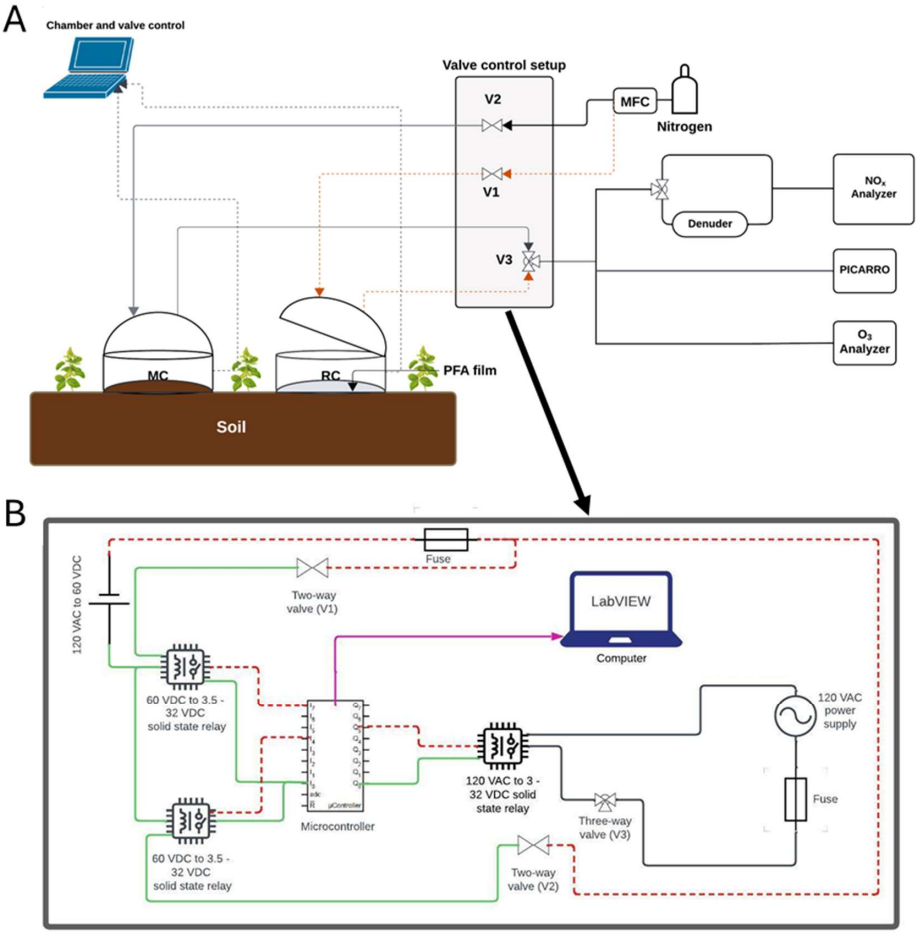

Figure 1. (**A**) Schematic of the dynamic chamber system to measure N_r and GHG fluxes. The components of the system include: the chambers, a dilution gas source (nitrogen (N_2) or zero air (ZA)), solenoid valve control, gas transfer lines, and gas analyzers. Grey lines indicate dilution gas flow from a source (e.g. cylinder) to the measurement chamber (MC) and air sampled from the MC to the analyzers. The dashed orange line represents these same flows relative to the reference chamber (RC). Communication lines from the chambers to a computer for automated control and ancillary sensor data collection using the chamber software (eoslink-AC; blue dotted lines). (**B**) The valve control setup for flow control in the complete dynamic chamber system, illustrating electrical components and lines needed for full automation using LabVIEW. It includes two 24 V DC two-way valves (V1 and V2; red dashed lines for negative electric potential, green for positive), with power supplied by solid-state relays, and a three-way 120 V AC valve (V3; black lines) with a power supply and another solid-state relay. The purple arrow represents the USB data acquisition connection from the microcontroller to a computer running the LabVIEW VI for valve control.

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Reactive gases require continuous correction for surface interactions and/or transformations as ambient levels are dynamic, so the RC component of this system design continuously baselines the physical interactions and chemistry happening on its surfaces both before and after quantifying reactive gas fluxes with the MC. 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 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 2.6). The resulting accumulated mixing ratios of HONO in the chamber are well above the 1.4 parts per billion (ppbv) mixing ratio detection limit (LOD) of even a modified NO_x analyzer, such that it can be used for measuring HONO (Crilley et al., 2023; Lao et al., 2020; Zhou et al., 2018; Nodeh-Farahani et al., 2021).

Headspace recirculation to facilitate analyte mixing ratio enhancements for non-destructive spectroscopic GHG analysis is a common measurement approach to decrease flux observation times. Reactive nitrogen measurements, in contrast, are typically destructive techniques that change the identity of the target analyte in the act of quantifying its abundance. To interface with such instruments, the sampled air needs to be replaced (Linde Canada Plc, PN: NI LC250-230) to balance the flow demand in a closed chamber. This balance is delicate even when using mass flow controllers (MFCs) on both incoming and outgoing flows, and the best solution we identified is to provide a slight overflow that takes advantage of the chamber design to vent excess pressure through a short length (~15 cm) of 1/8" ID, ¼" OD tubing that keeps the internal pressure equivalent to ambient. The flow differential between make-up gas and sampling is roughly 400 $cm^3\ min^{-1}$. Such a supply of make-up gas was explored across a range of potential flow rates when using destructive gas analyzers (e.g., three instruments each sampling at 1 - 4 standard litres per minute, L min^{-1}) to find that 6 L min^{-1} is the upper limit of flow-through where the chamber pressure is not substantially perturbed from ambient and the chamber lid retains its seal.

In the field, a flux measurement cycle begins with closing the RC while the MC is open. At defined intervals, they alternate their open-closed states. Flows of make-up gas to each chamber are modulated with a pair of two-way solenoid valves. When sampling from the RC, one valve (V1; Figure 1) is open to permit make-up gas flow while the other valve (V2) is closed to prevent the flow from being directed to the MC. On the sampling lines, a three-way solenoid valve (V3)

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alternates to guide flow from whichever is closed to the suite of gas analyzers. In this work, the gas instrumentation included a modified NO_x chemiluminescent analyzer (NO, NO_2, and HONO), a greenhouse gas and ammonia cavity ringdown spectrometer (H_2O, CO_2, CH_4, N_2O, NH_3), and a UV-absorption ozone (O_3) analyzer. All instrument and operational details are provided in Section 2.3.

2.1.2 Automated controls: system, data collection and processing

The chamber eosLink-AC software (Eosense Inc., Dartmouth, NS) is used to define the duration of chamber opening and closing cycles, and logs chamber temperature, pressure, and auxiliary sensor data associated with a given eosAC-LT chamber. Each chamber requires a 12 V DC power supply connected by USB to a laptop through a weatherproof communication cable, controlling the chamber lid and data transfer.

When a chamber cycle begins, a text file is generated and includes measurement time elapsed, chamber lid status, chamber temperature and pressure, and auxiliary sensor data. This data file is updated at least once every 10 seconds, varying between 2-8 second intervals, which we average onto a 1-minute time base to match measurements from the slowest gas analyzers. The solenoid valves are modulated by the electrical circuit shown in Figure 1B. Automation is facilitated by a microcontroller (NI-6509i, National Instruments) programmed with a custom-scripted LabVIEW VI (LabVIEW version 2020). The VI controls valve states (i.e., for V1, V2, and V3) and synchronization of the valve switching with respect to each chamber opening and closing cycle as described in the previous section. The VI also generates its own text file containing valve open/close state and a timestamp to be used for data processing. A custom R script (R Studio v3.0.1) was developed to process the data file generated by eoslink-AC, data from all reactive gas analyzers, and the VI. Further design information and full details of this sampling strategy and script can be found in Section S1 of the supporting information, and is available on the GitHub repository alongside our VI (https://github.com/fjs-vdblab/fluxchamber.git).

2.1.3 Reactive and greenhouse gas instrumentation for flux measurements

The mixing ratios of NO and NO_2 were measured using a commercially available chemiluminescent NO_x analyzer (EC 9841, American Ecotech, Warren, RI). The calculated LOD

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determined from sampling dry zero air was 0.84 ppbv, 0.67 ppbv and 1.07 ppbv for NO, NO_x, and NO_2, respectively. The instrument has an operating range of 0 – 20 parts-per-million by volume (ppmv), a sample flow rate of 0.5 L min^{-1}, and reports measurements at a time resolution of 1 minute. To quantify NO_2, it is reduced to NO on a heated molybdenum catalyst (325 °C). To prevent interferences 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.

A commercial O_3 analyzer (Serinus 10, American Ecotech, Warren, RI) was used to measure mixing ratios, quantify O_3 loss to surfaces, and constrain the reaction of O_3 with NO to form NO_2 in the pilot study sampling. This analyzer employs a non-dispersive UV absorption cell to quantify O_3 in the sampled air. The calculated LOD from sampling zero air is 0.95 ppbv at 1 minute time resolution, with an operating range of 0 to 20 ppmv and a sampling flow rate of 0.5 L min^{-1}. Quality control procedures for the NO_x and O_3 instruments can be found in Section S2.

The mixing ratios of greenhouse gases (GHGs) and ammonia (NH_3) sampled from the automated chamber system were measured using a Picarro G2509 which uses cavity ring down spectroscopy (CRDS) to simultaneously measure nitrous oxide (N_2O), methane (CH_4), carbon dioxide (CO_2), and NH_3 at ppbv levels, as well as water (H_2O) vapor at ppmv. The analyzer has a time response of ~ 8 seconds for N_2O, CH_4, CO_2, H_2O and < 2 min for NH_3. The Picarro G2509 instrument was used for measurements during both the lab experiments and the pilot study campaign. The customized version of the instrument had a sampling flow rate of ~0.23 L min^{-1}, and was equipped with an inlet filter. To minimize adsorption and chemical interactions of NH_3 on instrument surfaces, stainless steel gas handling components, including the inlet bulkhead, were replaced with PFA counterparts. The instrument cavity material was treated with a SilcoNert® coating by the

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manufacturer. The Picarro G2509 analyzer utilizes cavity ringdown spectroscopy to quantify the mixing ratio of the target analytes, and a full span calibration is not necessary to be performed regularly. Despite this, we validated its calibration and performed quality control checks in our laboratory to ensure the accuracy and stability of the analyzer for all aspects of this work presented below (Section S2).

2.2 Chamber modifications to minimize NO_2 reactions on chamber surfaces

To transfer reactive gases through these chambers, interactions with surfaces need to be limited at all points of potential adsorptive or reactive losses. The custom-made base plate, consisting of two rings made from PTFE sheets with a PFA film pinned between them (Figure S1) was used to assess gas interactions on chamber surfaces and acts as the RC for field measurements. From this starting point, commercial components were identified for replacement. First, the gas inlet and outlet push-to-connect fittings in the original chamber configuration have plastic grips, with an internal component made of brass, which is informally known in the atmospheric chemistry community to have strong interactions with nitrogen oxides. These brass fittings were replaced with PTFE Swagelok® bulkhead fittings (PN: T-400-1-4) as shown in Figure S2. Similarly, the polyacrylate wall and lid surfaces of the chambers were considered, which are, by design, actinically transparent to ensure PAR is transferred to any contained plants or surfaces. To retain this visible radiation transparency, while also making the surface more inert, we applied 0.002” thin PFA film to the inner surfaces using double-sided tape (Figure S2).

2.3 Chamber modification validation using greenhouse and reactive gases

The design of the chambers by the manufacturer is to transfer GHGs to non-destructive gas analyzers by recirculating the headspace. Before and after our modifications, we had to ensure that the non-reactive GHGs were still transferred through the system. In addition, we challenged the transfer of N_r gases by controlled gas delivery. It was expected that N_r gases could undergo interactions and/or chemical transformations on the chamber surfaces and sampling tubing that would differ between the unmodified and modified variants. Determining the time constants of fill (E1, E2) and decay (E3, E4) of these reactive gases in the chamber allowed us to contrast their behaviour against that expected from a modelled theoretical inert trace gas in our system (Figure

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2). Equations used to model mass transfer in our chambers were derived from Pape et al. (2009). The resulting accumulation curve was modelled by the theoretical function:

$$\mu_{fill}(t) = 1 - e^{-\left(\frac{t}{\tau_{fill}}\right)} \quad \textbf{(E1)}$$

$$\tau_{fill} = V/Q_{fill} \quad \textbf{(E2)}$$

Where μ_{fill} represents the normalized mixing ratio of the gas in the chamber at the time t (min) after closing of the chamber compared to the maximum mixing ratio within the measurement cycle, τ_{fill} is theoretical accumulation timescale for transfer of an ideal inert gas (min), V is the volume of the chamber (0.072 m^3), and Q_{fill} represents the total experimental flow rate (2 L min^{-1}). Similarly, the theoretical decay curve when emptying the chamber can be obtained, where τ_{emp} is the theoretical decay timescale for gas transfer (min) and Q_{emp} is again the total experimental flow rate (2 L min^{-1}).

$$\mu_{emp}(t) = e^{\left(-\frac{t}{\tau_{emp}}\right)} \quad \textbf{(E3)}$$

$$\tau_{emp} = \frac{V}{Q_{emp}} \quad \textbf{(E4)}$$

2.3.1 Instrumentation and materials for control experiments

Control experiments for the transmission of inert and reactive gases were conducted by filling and emptying the chambers with known quantities of the target gases at mixing ratios relevant to the atmosphere, as well as in quantities that would accumulate during real observations of modest fluxes (e.g. from a fertilized farm field). Measurement of NO, NO_2 and HONO was performed using the modified NO_x analyzer, the GHGs (CO_2, CH_4 and N_2O) and NH_3 with the Picarro G2509, and O_3 with the UV-absorption instrument. Details of the generation of gas concentrations can be found in Section S3 of the SI.

2.3.2 Filling and emptying experiments with N_r, O_3, and GHGs

The positive control experiments filled the chambers in both modified and unmodified configurations, where the time constants were calculated from the measurements to compare against a theoretical inert and perfectly transferred gas (i.e. lost by dilution and removal to analyzers only). In each filling experiment, the chamber was flushed with pure N_2 from a liquid N_2 dewar (Linde Canada, PN: NI LC250-20) until a stable baseline level of each gas mixing ratio

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was reached; typically, these were values at the analyzer detection limits. Then, a blend of GHGs or one of the N_r analytes was delivered into the chamber along with N_2 as the dilution flow at a total flow rate of 2 L min^{-1}, and this was then sampled at a total of 1.8 L min^{-1} by the analyzers (Figure S4). The gases were added to the chamber from their respective calibration sources until the observed concentration (C) reached the known value being delivered (C_0), within error. Since different mixing ratios of the gases were added for these control experiments, the use of normalized concentrations was necessary to facilitate data analysis and visualization. Where surface interactions could be identified (e.g. for NH_3), the role of surfaces versus air exchange has been explored using double exponential fits (see ES-1 and ES-2 in Section S3) (Crilley et al., 2023; Ellis et al., 2010; Moravek et al., 2019). The gases were emptied back to the initial baseline level observed with clean dilution gas before starting the next replicate or a new filling experiment with a different target gas. Time constants for filling and emptying were then determined by fitting the experimental observations in Igor Pro8 (Wavemetrics, Portland, OR, US).

Similarly, the Eosense eosMX multiplexer is designed to coordinate chamber flux measurements using eosAC chambers with non-destructive analyzers, such that headspace can be recirculated while the chambers are closed. One of these devices was characterized for the transmission of GHGs and N_r gases, alongside similar modifications. This system is appealing as it has the eosLink-MX software (Eosense, V1.9.07), which is used for communication, scheduling actions, and logging peripheral data from all connected eosAC chambers. It features dedicated chamber tubing inlets and outlets, along with a COMM port supporting up to 12 eosAC chambers. Each chamber channel includes two Swagelok gas fittings for transporting gases to analyzers and for either recirculating, or in the case of N_r measurements, supplying a purging gas to the chamber headspace.

To optimize the performance for N_r species, the original stainless-steel (SS) Swagelok fittings and solenoid valves were compared against replacement PFA tube fittings, bulkhead unions (Swagelok, PFA-420-61), and a PTFE 3-way valve (Clippard, NR1-2-12-G2). A 2 L min^{-1} flow of dry zero air containing the target compounds was passed through either the SS valve with SS fittings or the PTFE valve with PFA fittings for 30 minutes each. The flow was measured before and after the valves to ensure the setup was free of leaks. The ratio of the transferred gas amount

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to the nominal was used to identify impacts of surface interactions on quantitative transmission to downstream gas analyzers. Further details are presented in Section S4.

2.4. Characterization of NO_2 loss on chamber surfaces

All losses of NO_2 in the chamber were characterized by the addition of known NO_2 mixing ratios to the chamber under a variety of relevant conditions (Figure S5). The experiments were performed progressively, starting from the unmodified configuration of the chamber, replacement of fittings, and covering the inner surface with PFA film to quantify their efficacy in minimizing NO_2 loss and/or transformation on chamber surfaces.

Different RH values were produced inside the flux chamber by combining flows of dry zero air (ZA) and one saturated with water vapour by transiting a 500 mL Pyrex impinger filled with deionized water (e.g. equal 1 L min^{-1} flows combine to an RH of 50%). A high-precision, research-grade humidity probe (HMP60, Vaisala Oyj, Finland; ± 3% at 0 - 90% RH, ± 5% at 90 – 100% RH) was connected to the chamber to confirm the set point by measurement in the chamber. The flow from an NO_2 calibration cylinder (Linde Canada; PN: NI NX5MC-AQ; 5.9 (±5%) ppm) was adjusted using an MFC and combined with a dilution flow of ZA to achieve mixing ratios of 5, 7 and 10 ppbv. The total flow rate for these experiments was 2.0 L min^{-1} and a vacuum pump (62.3 L min^{-1}, PN: UZ-07061-22, Gast Manufacturing Inc., Benton Harbor, MI, USA) with an MFC (10 L min^{-1}, PN: 1179C01314CR1BV, MKS instruments Inc, Andover, MA, US) was used to make up the sampling flow beyond the 0.5 L min^{-1} of the NO_x analyzer. The same flow difference stated above was maintained in the chamber, using the built-in vent.

Quantification of NO_2 and HONO in the air sampled from the chamber can be achieved using the alternating solenoid setup depicted in Figure S5. The sampled air is switched between two channels – one directly to the NO_x analyzer and the other through a Na_2CO_3-coated denuder – modulated every 5 minutes by a three-way solenoid valve (Fluoroware Galtek 1/4" F-NPT 3-way solenoid valve, 115V, PN: 203-3414-415. Entegris Inc., MN, US). When the sampled air flows directly to the analyzer, the total mixing ratio of NO_2 and acidic NO_y species, like HONO and HNO_3, is measured and has been termed NO_2^* (Crilley et al., 2023; Lao et al., 2020; Zhou et al., 2019). When the flow is directed through a Na_2CO_3 denuder, it selectively scrubs HONO and HNO_3, leaving behind NO_2 (Possanzini et al., 1983). Under the controlled NO_2 composition used in our experiments, it is expected that HONO will be the only acid present in the sampled air, as such

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experimental systems have been thoroughly characterized by Finlayson-Pitts et al. (2003),, and HNO_3 is retained on the surfaces (R3) (Barney & Finlayson-Pitts, 2000; Huang et al., 2002; Kamboures et al., 2008). As a result, by the differential measurement of mixing ratios recorded in the two channels (E5) every 5 minutes, HONO can be quantified.

$$HONO = NO_2^* - NO_2 \qquad \textbf{(E5)}$$

To quantify the amount of NO_2 lost to the chamber surface relative to the mixing ratio of NO_2 added to the chamber during an experiment, the NO_2 loss fraction (f_{NO2}) is informative for mass balance between the two processes. Comparison of each chamber modification on f_{NO2} helps identify which changes are essential in minimizing losses. Experiments using 5 ppbv of NO_2 at 85% RH added to the chamber were used to quantify f_{NO2} in the unmodified configuration (n=3), to derive an upper limit of irreversible loss to surfaces or chemical loss via surface hydrolysis (R3). Following the materials characterization experiments, additions of atmospherically relevant 5, 7 and 10 ppbv mixing ratios of NO_2 at three different RH values (45%, 65% and 85%) to the fully modified chamber were used to characterize and develop a correction methodology for the surface loss. The mixing ratios of NO_2 and RH values selected for these experiments are representative of the ambient atmosphere in urban areas (Toronto North Station, ECCC), where the chamber system was envisioned to be deployed.

2.5 Drivers of O_3 loss to chamber surfaces

We tested how modifications and aging of the interior chamber surfaces affected O_3 transfer. It is among the most sensitive/reactive species to transfer through this new system and is expected to drive reactive loss of NO when measuring N_r fluxes. The fraction of O_3 lost to chamber surfaces was first quantified using a clean and unmodified chamber with PTFE bulkhead fittings replacing the push-to-connect brass fittings. Prior to O_3 addition, the chamber was flushed with ZA until the background level of O_3 was at the instrument detection limits. Three mixing ratios of O_3 of 150, 200 and 250 ppb generated by a GasCal 1100 dilution calibrator with integrated O_3 generator and photometer (American Ecotech, Warren, RI) and added to the chamber for 60 mins or until a constant concentration was reached. Two replicate runs of each addition level were performed.

The fraction of O_3 lost to chamber surfaces was quantified in duplicate on a modified chamber with the interior chamber surfaces covered by brand new 0.002” thick PFA film in a separate set of experiments. The same mixing ratios of O_3 were delivered in duplicate to the modified chamber

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operated for lab and field experiments, so that the PFA film had been attached to the inner surface of the chamber and exposed to ambient air for more than two years, with 15 days of continuous use in an agricultural field during our pilot study. In all three experiments, the lost fraction of O_3 was determined for each mixing ratio delivered.

2.6 Proof of concept N_r fluxes from agricultural soils

2.6.1 Soil sample N_r emissions for lab experiments

Randomized soil samples weighing 4-5 kg were collected into Ziplock bags from an eight-plot grid established for an agricultural field site in Lambton County, ON, Canada (43°09'36.0" N 81°55'48.0" W). The samples were used to investigate emissions in the lab with and without the addition of fertilizers. Individual and pooled samples from the field plots were used. Bulk soil samples were prepared for lab-based chamber measurements by removing debris, roots and seeds, followed by oven drying at 35 °C for 24-72 hours on a stainless-steel mesh tray covered with aluminum foil, to prevent alteration of the microbial community from exposure to unrealistic temperature regimes. After drying, samples were stored in Ziploc® bags at room temperature until use.

Ultrapure water (18 MΩ·cm; Milli-Q®, Sigma-Aldrich, St, Louis, US) was added to approximately 350 g of a dry soil sample to achieve ~28% volumetric water content (VWC). The soil sample was loaded into the chamber on a foil-lined tray, and the water content was measured using a soil moisture probe inserted fully into the sample (TEROS 11, VWC range for mineral soils: 0.00 – 0.70 m^3/m^3; accuracy: ± 0.03 m^3/m^3; resolution: 0.001 m^3/m^3, METER Group Inc., WA, USA). The chamber was then sealed against intrusion from room air, and dry ZA was added to the chamber during the drying period. A modified NO_x analyzer measured NO, NO_2 and HONO following our usual configuration, while the Picarro G2509 measured N_2O and NH_3 fluxes. Both instruments monitored unamended soil samples and others fertilized with urea ($CO(NH_2)_2$), ammonium carbonate (AC, $(NH_4)_2CO_3$), ammonium bicarbonate (ABC, NH_4HCO_3) at rates of 100 kg N ha^{-1}. A similar experiment was conducted with ammonium nitrate (NH_4NO_3) at the same fertilizer rate using only the modified NO_x analyzer. Soil VWC and headspace RH were recorded using auxiliary sensors within the chamber.

2.6.2 Field deployment of automated dynamic N_r chambers

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The RC and MC setup was deployed to make automated N_r flux measurements from the same agricultural field as the lab-based soil samples described in the prior section. The observations took place in early September 2022 at the end of a soybean cropping season. A detailed description of the campaign and its results is the subject of a separate work, so we provide a brief overview here relevant to demonstrating the utility and procedure of an RC/MC chamber pair to determine fluxes from field observations. The total measurement period was approximately two weeks in duration to test the performance of the designed system. Generally, conditions were hot and dry, without precipitation, and the soybeans surrounding the observed soils were undergoing senescence during the measurement period. The chambers were deployed only on the soil, between crop rows, and operated to quantify fluxes as outlined in Section S7. After an initial 7-day period of observing baseline fluxes from the field, an experimental perturbation was conducted to stimulate N_r emissions through the addition of an aqueous urea solution equivalent to 22 kg N ha^{-1} of fertilizer added by broadcast application, followed by washing into the soil by an equivalent of 2.5 cm (1") of rain. The modified NO_x analyzer and the Picarro G2509 were used to measure the N_r and GHG fluxes continuously across both periods.

2.7 Soil flux determination

The flux of a gas is the rate at which it is released and/or transferred across a surface or an interface (e.g., soil to atmosphere) per unit area per unit time. Gas fluxes are of high interest in agriculture as they give insight into the uptake or emission of N-bearing gases that may lead to fertilizing, or loss of fertilizing effects, respectively. Fluxes are also important for assessing the state of plants or soils at interfaces through metrics like primary productivity, in which case measurement of a GHG like CO_2 provides the insight (Anthony & Silver, 2024; Li et al., 2016; Okiti et al., 2025). 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, 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).

$$F_{\text{net}} = (\lambda).\left(\frac{V}{A}\left(\frac{\Delta C_m}{\Delta t_m} - \frac{\Delta C_r}{\Delta t_r}\right) + \frac{Q_{\text{out}}}{A}\left(\frac{\int_{t_{1m}}^{t_{2m}} c_m(t)\ dt}{\Delta t_m} - \frac{\int_{t_{1r}}^{t_{2r}} c_r(t)\ dt}{\Delta t_r}\right) - \frac{V}{A}\left(\frac{\int_{t_{1m}}^{t_{2m}} R_m(t)\ dt}{\Delta t_m} - \frac{\int_{t_{1r}}^{t_{2r}} R_r(t)\ dt}{\Delta t_r}\right)\right) \quad \textbf{E6}$$

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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; Q_{out} is the volumetric flow rate of air exiting the chamber (m^3 s^{-1}; $c_m(t)$ and $c_r(t)$ are target gas concentrations within the measurement and reference chamber (mol m^{-3}), respectively; $\frac{\Delta C_m}{\Delta t_m}$ and $\frac{\Delta C_r}{\Delta t_r}$ represent their corresponding rates of change (mol m^{-3} s^{-1}); and F_{net} is the resulting net gas flux per unit area (mol m^{-2} s^{-1}).The terms R_m and R_r denote the instantaneous chemical production or loss rate expressed in units of mol m^{-3} s^{-1} for consistency. The dimensionless attenuation factor λ is required to correct for interactions of reactive gases with chamber 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 and the target gas concentration from controlled deliveries integrated over the chamber closure interval as derived in Section S7. The attenuation correction removes bias from chamber-induced artifacts in flux estimates, so that more accurate soil–atmosphere exchange is reported.

$$F_{\text{net}} = \lambda \cdot \frac{P_{\text{air}}}{R \cdot T} \cdot \left(\frac{V}{A} \left(\frac{\Delta X_m}{\Delta t_m} - \frac{\Delta X_r}{\Delta t_r} \right) + \frac{Q_{\text{out}}}{A} \left(\frac{\int_{t_{1m}}^{t_{2m}} X_m(t)\ dt}{\Delta t_m} - \frac{\int_{t_{1r}}^{t_{2r}} X_r(t)\ dt}{\Delta t_r} \right) \right) \quad \textbf{E7}$$

For inert gases in E7**,** the fluxes can be based on mixing ratios, where X_m *and* X_r are the gas volumetric mixing ratios (mol X per mol air), P_{air} is the air pressure (Pa), T is the absolute temperature (K), and R is the universal gas constant (J mol^{-1} K^{-1}). By comparing the RC and MC observations, we isolate the effects of specific environmental conditions on N_r (E6) or GHG (E7) exchange fluxes, while accounting for surface effects and chemical transformations in the former.

3 Results

3.1 Determining time constants of reactive nitrogen and GHGs

The time constants of both filling and emptying the chambers were calculated using concentrations normalized to their initial values, for each N_r gas and GHG. These were used to quantify gas transfer times through the chambers and to confirm performance relative to theory. Where departures were identified, we quantified the extent of surface interactions for the various target analytes so corrections for determining in situ fluxes could be implemented (Table 1, Figure 2).

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3.1.1 Time constants of greenhouse gases (GHGs)

Determination of the GHG time constants allows benchmarking of the chamber performance prior to and after modifications, which then allows us to contrast the behaviour of transferred reactive gases through the chambers. In both the modified and unmodified chambers, the greenhouse gases CO_2, CH_4 and N_2O were anticipated to behave as non-reactive trace gases with little to no physical interactions on chamber surfaces, nor to undergo chemical transformations.

The theoretical fill and empty rates for the chambers with a flow rate of 2 L min^{-1} are 36 min. The average measured time constants of filling with the greenhouse gases CH_4, CO_2, and N_2O in the unmodified chamber were found to be 37 ± 1 min, 37 ± 2 min, and 37 ± 1 min, respectively (Table 1). During the emptying phase, the average time constants for CH_4, CO_2, and N_2O were 37 ± 1 min, 37 ± 1 min, and 38 ± 2 min, respectively. These measurements are not different from theory within the limits of experimental accuracy, demonstrating that GHGs do not deviate from the values modelled for an ideal trace gas (Figure 2). In either experiment, the time constants did not change in the presence of the chamber modifications. Since the GHGs are effectively transferred through both the modified and unmodified configurations of the chamber, the baseline performance of the chambers was not affected by the hardware modifications. Therefore, comparison of these results with the time constants of N_r gases provides a description of their interaction or transformation processes on the modified chamber surfaces.

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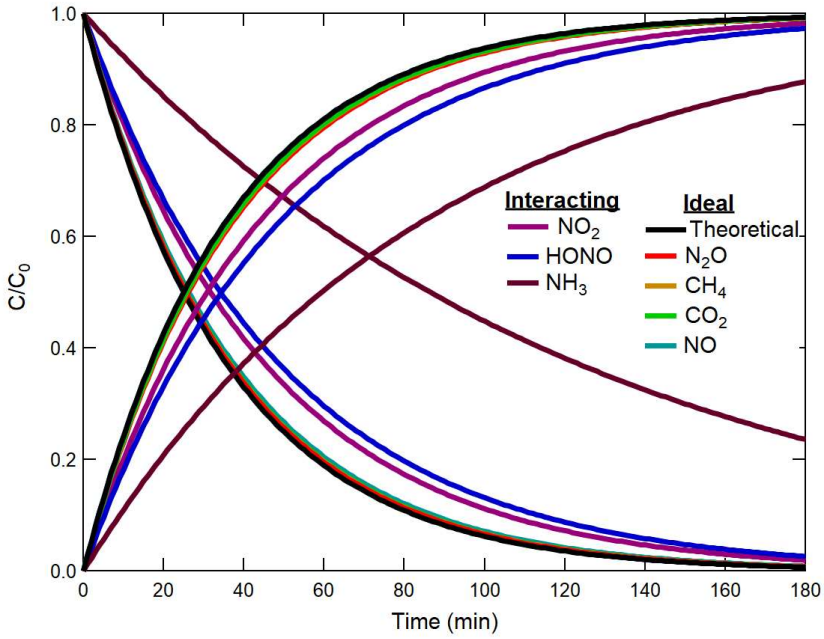

Figure 2. Addition of reactive nitrogen gases and greenhouse gases to a modified dynamic chamber. For clarity, the coloured traces show the fitting curves corresponding to the response time in concentration normalized to the delivered value of each gas while filling and emptying the chamber. The black trace corresponds to a perfect non-reactive transfer of an ideal trace gas based on volume transfer in the chamber only. Note that the N_2O, CH_4, CO_2 and NO fill and empty traces all overlap with the theoretical fill and empty curves.

3.1.2 Time constants of reactive nitrogen gases

In the modified chamber, the time constant of filling or emptying with NO was 38 ± 1 min. The obtained NO time constants are similar to GHGs, as NO is not expected to have strong surface interactions. 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 inlet line and the chamber, and (2) the adsorption and desorption of the gas onto and from the chamber surface (Whitehead et al., 2008). Increases in surface interactions were observed for increasingly polar gases in the order of NO_2, then HONO, and most for NH_3 (Figure 2). The highest change in the time constants between the modified and unmodified configurations was 2.6 ± 2.5 min, observed for HONO, with smaller improvements observed for NO_2 and NH_3 during the filling process. Improved time constants

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when emptying reactive nitrogen from the chambers had similar trends (Table 1).

Overall, the deviations for these gases to longer time constants than those expected from an inert molecule can be attributed to their polar, ionizable, and/or reactive nature. For example, NO_2 is lost more readily than NO, possibly through its known reaction on surfaces to make HONO and HNO_3, being lost itself in the process (Finlayson-Pitts et al., 2003). It also has higher water solubility than NO, but lower than for HONO or NH_3. Similarly, a decrease in transmission efficiency for HONO could be explained by its weakly acidic nature (pKa = 3.16) (Silva et al., 2006) and solubility in water (Henry's law constant = 0.48 mol/m^3 Pa; (Schwartz & White, 1981) that facilitate partitioning and dissociation in surface water films, which could generate non-volatile nitrite (NO_2^-) on chamber surfaces. This chemistry will slow the transfer of gas-phase HONO through the chambers, as the NO_2^- would need to protonate before being lost as neutral HONO when repartitioning to the gas phase (R4, R5). Finally, the most delayed transmission rate is for NH_3, likely because it undergoes strong inter-molecule interactions and ionization on the chamber surfaces and/or any interfacial water (Henry's law constant = 5.9x10^{-1} mol/m^3 Pa (Orkin et al., 2011); pKa = 9.25 (Lide, 2009), as well as on tubing surfaces and potentially partitioning into the tubing before reaching the analyzer (Pagonis et al., 2017).

The determined surface impact values (D; Table 1) 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 when the surface has been exposed and equilibrated with the analyte, which is commonly referred to as passivation. As a result, increasing delays from NO through NH_3 exist in our N_r gas suite due to increasingly stronger interactions with chamber surfaces and gas handling lines. For NH_3 specifically, the fill has a D value of 89%, while during emptying it is only 23%. This is due to all sample handling surfaces not being passivated prior to filling, similar to our findings with NH_3 transfer for other N_r instruments (Crilley et al., 2023). In contrast, during the emptying process, desorption occurs over previously exposed surfaces ending at the instrument, reducing the extent of surface effects. 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

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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. In addition, minimizing the potential for transformations reduces the frequency required for in-field characterization of these processes through positive and negative gas delivery controls. 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.

Table 1. Summary of time responses of addition and removal of GHGs and N_r gases to and from a chamber at 2 L min^{-1} in unmodified and modified configurations. Time responses here correspond to a theoretical fill or empty e-folding time response of 36 minutes. Where analytes were observed to undergo surface interactions, a double exponential fit was used to characterize them, with the first time constant representing the known gas exchange rate being fixed at 36 minutes, as this was observed for the non-reactive gases, and the second time constant is reported (*) alongside an assessment of the relative magnitude of surface interactions, through the D-value (%) (Crilley et al., 2023; Ellis et al., 2010; Moravek et al., 2019). Variability shown is one standard deviation of the mean from replicate experiments (n=3).

Gas species	Direction	Unmodified (min)	Modified (min)	Improvement (min)	D (%)
NO	Fill	38.8 ± 0.7	37.8 ± 0.6	1.0 ± 0.7	-
	Empty	37.9 ± 1.5	36.0 ± 0.6	1.9 ± 2.1	-
NO_2	Fill*	18.9 ± 0.6	18.0 ± 3.1	0.9 ± 3.2	94 ± 18
	Empty*	21.2 ± 1.2	20.4 ± 1.4	0.8 ± 1.9	78 ± 21
HONO	Fill*	21.9 ± 1.1	19.3 ± 1.2	2.6 ± 1.6	74 ± 10
	Empty*	23.2 ± 1.4	21.2 ± 0.9	2.0 ± 1.7	71 ± 9
NH_3	Fill*	69.6 ± 0.4	68.2 ± 0.5	1.4 ± 0.6	89 ± 3
	Empty*	76.9 ± 0.8	75.0 ± 4.6	1.9 ± 4.7	23 ± 4
CO_2	Fill	37.9 ± 1.5	37.0 ± 1.8	0.9 ± 2.3	-
	Empty	38.0 ± 1.8	37.0 ± 1.2	1.0 ± 2.2	-
CH_4	Fill	37.9 ± 1.1	36.8± 1.2	1.1 ± 1.6	-
	Empty	39.1± 1.7	37.2 ± 1.2	1.9 ± 2.1	-
N_2O	Fill	38.6 ± 2.1	36.7 ± 1.2	1.9 ± 2.4	-
	Empty	39.7 ± 1.3	37.7 ± 1.6	2.0 ± 2.1	-

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3.2 Multiplexer modification impacts on gas transfer

The multiplexer (eosMX; Eosense Inc.) allows us to operate up to twelve dynamic chambers simultaneously with a suite of gas analyzers such as the Picarro G2509, NO_x, and O_3 analyzers. However, the commercial multiplexer is constructed with stainless steel (SS) valves and fittings that would be expected to facilitate strong interactions or losses of target gases in the N_r analyte suite. Valves and fittings made of SS have a higher tendency to chemically interact and/or adsorb reactive gases compared to fluoropolymer replacements. To address this uncertainty, the gas transfer efficiency as a percentage loss in the multiplexer versus a bypass line was evaluated specifically for NH_3 and NO_2, alongside standard GHGs as they passed through fittings and gas handling solenoid valves made of SS or PFA and PTFE replacement parts.

The loss fractions were modest and measurable when connected to the analyzers using minimal lengths of PFA tubing (~50 cm). The most substantial loss of gases was observed on SS, in which the highest reactivity and/or adsorption were expected due to its known tendency to interact with reactive gases (Vaittinen et al., 2014). When the GHGs were delivered after dry zero air into the SS setup for 30 minutes, typical of a chamber closure period, their losses ranged from 10% for N_2O to 19% for H_2O. Meanwhile, NO_2 exhibited 17% loss on the SS surfaces, and the greatest effect was seen for NH_3 with a loss of 38% (Figure S6). In contrast, losses on the chemically inert and hydrophobic surface of the PFA fittings and PTFE valve were negligible (<1%) for most gases, except for NH_3, which still exhibited a measurable loss of 11%. Other reports have also shown up to 15% loss of NH_3 at atmospheric pressure on PTFE and PFA surfaces (Ellis et al., 2010; Shah et al., 2006; Vaittinen et al., 2014). While it is expected that the SS would eventually passivate and improve the transmission of the GHGs in a standard recirculation approach, this is not likely to be the case for destructively analyzed N_r and even more so if it facilitates a chemical transformation. Overall, we found that replacing the multiplexer SS valves and fittings with PFA fittings and PTFE valves provided a 9–27% reduction in surface losses of N_r compounds and GHGs. We strongly recommend the use of PTFE and/or PFA materials over SS for more accurate measurement of N_r species when interfacing the dual chamber setup with the destructive N_r analyzers needed for field flux measurements, whether using a custom setup of the commercially available multiplexer.

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3.3 Minimizing NO_2 losses and determining controlling variables

In addition to the rate of transfer of N_r gases, chamber modifications are necessary to prevent reactive losses. The lost fraction of NO_2 (f_{NO2}) to chamber surfaces was quantified by the addition of known mixing ratios of calibration gas to the chamber in both the unmodified and modified configurations under atmospherically relevant humidities. These experiments enabled us to determine the magnitude of NO_2 lost to the chamber and gas transfer tubing surfaces due to chemical and/or physical transformations, as well as demonstrate the effectiveness of the different chamber modifications in minimizing these losses. For NO_2, a probable chemical transformation pathway is its heterogeneous conversion to HONO (R3), which is favourable under atmospherically relevant humidities, and the resulting water-adsorbed surfaces expected to exist throughout the chamber and sampling lines.

3.3.1. Chamber modification impacts on NO_2 losses

The average fractional loss (f_{NO2}) for an unmodified chamber and one modified with the PFA film and PTFE bulkhead fittings was measured under conditions of 83% RH and 5 ppb of NO_2. Substantial reduction in NO_2 loss and transformation was observed from the implemented modifications. In the original unmodified configuration of the chamber, f_{NO2} was 0.36 ± 0.02 (Figure S7). When the interior chamber surfaces were covered with a film of PFA, it was reduced to 0.22 ± 0.03, a relative decrease of 18%. This is consistent with the acrylic chamber surfaces and fasteners to the chamber frame, facilitating physical and/or chemical loss of NO_2.

The film of PFA, along with other fluoropolymers, is known to have excellent chemical resistance and low reactivity towards a range of chemicals, including NO_2 (Ebnesajjad, 2005; Graham et al., 1997). In addition, the superhydrophobic nature of these materials prevents the accumulation of water on the surfaces, which is known to facilitate atmospheric surface reactions of NO_2 (Finlayson-Pitts et al., 2002; Jenkin et al., 1988; Stutz et al., 2002) and create analytical bias in the measurement of trace gases like HONO, especially when instrument gas sampling inlets do not take this into account (Crilley et al., 2019; Von Der Heyden et al., 2022).

The replacement of the brass-lined push-to-connect bulkhead fittings with PTFE led to a similar decrease in f_{NO2}, which was reduced by 17% to a final value of less than 0.05 ± 0.02 (Figure S7). These fitting surfaces act as the largest surface-driven NO_2 loss despite their surface area being

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very small compared to that of the entire chamber configuration and with a very small contact time against the gas sample (0.012 s per fitting at a flow rate of 2 L min^{-1}).

The loss of NO_2 in the commercially available system is challenging to attribute solely to the heterogeneous hydrolysis reaction. During the characterization experiments, the conditions inside the chamber were matched to those reported by previous lab studies, which have shown that high RH, presence of NO_2, and surface adsorbed water on surfaces favour this loss mechanism (Jenkin et al., 1988; Stutz et al., 2004). The reaction is known to occur on surfaces such as Pyrex (Jenkin et al., 1988) and borosilicate glass (Finlayson-Pitts et al., 2002), but no prior studies to date, nor this study, have demonstrated metallic surfaces as facilitating this mechanism.

Overall, chamber modifications were effective in minimizing NO_2 losses. The inert PTFE fittings dramatically minimized transformations, while PFA film lining the inner chamber surfaces was also effective, but less so. Our results indicate that water-adsorbed and metallic surfaces, such as brass, facilitate substantial loss and/or transformations of NO_2. Further investigation is required to confirm the mechanism(s) at play and is beyond the scope of this work.

3.3.2. RH-facilitated NO_2 loss as a function of concentration

A complete characterization of f_{NO2} and the amount of HONO in the fully modified chamber was determined under a range of environmentally relevant RHs and NO_2 concentrations. We found that the absolute and fractional NO_2 losses were highest under the highest RH conditions (85%; Table 2). However, the f_{NO2} does not appear to follow a concentration-dependent trend across the additions made at lower RHs, with at most 0.4 ppbv NO_2 lost across the remainder of the tests, a value which is equivalent to the LOD of the NO_x analyzer used. This would generate 0.2 ppbv of HONO according to the disproportionation of the hydrolysis mechanism, which is well below the analyzer detection limits. Overall, the modifications successfully reduce NO_2 losses below 10% across all environmentally relevant conditions the chambers are expected to encounter, with our findings here suggesting that the mass lost is nearly constant and independent of NO_2 mixing ratio at RHs below 85%, while being marginally higher at and above this value.

Quantifying f_{NO2} and the amount of HONO made in the chamber is required for the correction of field datasets. Quantifying NO_2 loss to the chamber surfaces allows us to prevent bias when

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reporting NO_2 exchange processes on environmental surfaces, as the magnitude of the losses attributed to chamber surfaces versus the surface studied can be corrected. The system, via the reference chamber, can also quantify any changes in these processes over time if standard concentration additions to the headspace are conducted. Consequently, important parameters such as NO_2 deposition fluxes on surfaces can be better estimated (Pape et al., 2009).

Since the inferred HONO mixing ratios from the chamber surfaces across various environmental RHs are nearly invariant at 0.2 ± 0.1 ppbv, it is simple to background correct any observational datasets by subtracting this amount from the total HONO measured in the chamber if a more sensitive analyzer is used during field or lab experiments. In addition, as the NO_2 values expected in most atmospheric gas samples during field measurements are well into the ppbv range (>3.3 ppbv per 30-minute flux measurement for a 1.4 ng m^{-2} min^{-1} emission), the corrections would be easy to implement in post-processing of datasets and have minimal impact on the technical aspects of the analytical determinations.

Table 2. Characterization of NO_2 lost in the modified chamber under environmentally relevant ranges of NO_2 and RH. The loss fraction (f_{NO2}) and HONO produced in the chamber were quantified at each of three NO_2 mixing ratios (5, 7, 10 ppbv) delivered at varying relative humidities (RH) to the fully modified chamber. Variability (±) provided is one standard deviation of the mean from replicate experiments (n=3).

RH (%)	NO_2 added (ppbv)	NO_2 lost (ppbv)	f_{NO2}	HONO produced (ppbv)
85	5	0.50 ± 0.01	0.1 ± 0.02	
85	7	0.70 ± 0.04	0.1 ± 0.02	
85	10	0.50 ± 0.07	0.05 ± 0.01	
65	5	0.30 ± 0.10	0.06 ± 0.02	
65	7	0.40 ± 0.09	0.06 ± 0.02	<1.1[a]
65	10	0.30 ± 0.08	0.03 ± 0.01	
45	5	0.30 ± 0.05	0.05 ± 0.01	
45	7	0.40 ± 0.04	0.06 ± 0.00	
45	10	0.30 ± 0.08	0.03 ± 0.01	

[a] – below instrument detection limit of 1.1 ppbv determined as S/N=3 while sampling zero air

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It should be noted that the amount of HONO in the chamber was below the LOD of the NO_x analyzer for HONO (1.07 ppbv), meaning that the upper limit of HONO inferred may perhaps, in fact, be negligible. Therefore, future experiments that wish to detect small N_r fluxes accurately will need to focus on reproducing these experiments with a higher performance instrument, such as a time-of-flight chemical ionization mass spectrometer (ToF-MS) or long-path absorption photometer (LOPAP), which have lower detection limits (Crilley et al., 2019; Lee et al., 2014; Neuman et al., 2016; Reed et al., 2016).

3.2.3 Characterization of O_3 loss in the chamber modified with and without PFA

Ozone loss was observed in both modified and unmodified chamber configurations, with 18% lost to clean lines alone when transferring 30 ppbv. The unmodified chambers lost 45% across all delivered mixing ratios (150-250 ppbv), which are higher than those typically expected in ambient air. This was reduced to 35% when the fluoropolymer modifications were implemented with new clean PTFE fittings and PFA film. When the PFA film was aged by 15 days of ambient sampling and 2 years of exposure to lab air, the losses were substantially exacerbated, reaching 80%. Such outcomes are expected and can be attributed to several factors, primarily involving surface reactions with built-up films of deposited organics, adsorption, and material interactions (Burkholder et al., 2015).

Ozone is known to undergo heterogeneous surface reactions, particularly on materials like glass, metals, or polymers (Plake et al., 2015). These surfaces often contain reactive sites such as hydroxyl groups or adsorbed water molecules that can catalyze the decomposition of O_3 into molecular oxygen (O_2) and other byproducts (George et al., 2015). Adsorption of O_3 on chamber surfaces is another potential pathway for loss. When O_3 molecules interact with surfaces, they may undergo a reaction if the materials are not inert. The use of PFA here was intended to benefit the transfer of O_3, yet despite its high chemical inertness, low reactivity, and resistance to the uptake of many chemicals from gas samples, the subsequent O_3-driven surface reactions are still substantial (Ebnesajjad, 2017). This is likely because, over time, reactive substances from sampled air accumulated through adsorption on the PFA film and/or its defect sites, thereby reducing its effectiveness. The same issue is well-known for PFA tubing used in standard air quality monitoring and is a common maintenance need for O_3 analyzer inlets. Further, physical wear or surface aging might alter the material surface through product formation or exposure of new reaction sites, which

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makes it less resistant to further reaction with O_3, and therefore increases the rate of loss over time. This is the case in our aged PFA film results, which emphasizes the importance of regular replacement of the film as part of the N_r system maintenance and that quality control procedures characterizing the chamber material performance with respect to O_3 will provide the highest accuracy of experimental results.

3.3 Proof-of-concept reactive nitrogen fluxes using soil samples in the lab

Proof-of-concept flux measurements were performed using the modified dynamic chamber system to demonstrate that emissions of N_r gases from agricultural soil samples can be measured under controlled conditions, similar to many prior reports using custom-built soil chambers (Almand-Hunter et al., 2015; Pape et al., 2009; Tang et al., 2019, 2020).

3.3.1. Fluxes of NO, NO_2, and HONO from agricultural soil samples

Emission fluxes were measured from two pooled and two individual soil samples collected from a single agricultural field (Table 3; Section S6). The average and integrated fluxes of N_2O, NH_3, NO, NO_2, and HONO were assessed under controlled, environmentally realistic, drying conditions of zero air modified to be 65% RH delivered at 3.6 L min^{-1} to the chamber headspace where the soil was contained. The soil started the drying process from a VWC of approximately 25% with the flows held constant for around 4 days or until the VWC reached 15% (Table 3).

As the soils dried, NO and NO_2 emissions increased, with NO fluxes highest across all replicates and reaching up to 2.50 µg N m^{-2} hr^{-1}. This trend is consistent with the prior work of other researchers, showing peak NO emission potentials when VWC drops below 25% during soil drying, which is when microbial nitrification and denitrification processes are suggested to become more active (Bao et al., 2022; Oswald et al., 2013). The soil VWC at which these maxima occur can vary depending on soil type, texture, and the microbial diversity therein (Ludwig et al., 2001; Schindlbacher et al., 2009). The plot-level replicates from our field had a higher integrated NO flux (i.e., > 2600 µg N m^{-2}), compared to the pooled replicates (<1000 µg N m^{-2}), likely indicating real differences in preserved microbial hotspots, intact plot-level soil aggregates, true spatial variability, and plot-specific N availability (Table 3). Soil texture and aggregate size, for example, play an important role in building the porous structure of soil, which has implications for the

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release of gases (Mangalassery et al., 2013). Soil aggregates, therefore, govern the release of gaseous N_r analytes like NO based on the aerobic or anaerobic state of the soil. Here, our low level of soil manipulation (i.e. not ground, no sieving) will drive some of the variability by preserving these features, which exist across and within real soil systems (Lipiec et al., 2007). Individual plot samples also retain plot-specific microbial communities when working with intact soil, whereas soil grinding can temporarily inhibit microbial activity. While we tried to minimize soil handling and processing extremes in these experiments, a measure of homogeneity was also pursued, and fully intact soil cores were not assessed.

Integrated NO_2 fluxes showed the same trend, with more sample-to-sample variability as one pooled replicate (R2) produced over three times the emissions of R1, despite both experiments being conducted across identical moisture content ranges (Table 3). Given the limited studies directly measuring NO_2, such as Purchase et al. (2023), this variability is difficult to interpret and highlights the need for more assessments of its production pathways and controls, which our developed chambers show promise for.

The observed average HONO fluxes remained low across all of the samples, ranging from 0.05 to 0.25 µg N m^{-2} hr^{-1} (Table 3). These values are lower by up to an order of magnitude compared to those reported in other controlled laboratory studies, where HONO fluxes ranging from 250 ng N m^{-2} s^{-1} to 900 µg N m^{-2} hr^{-1} have been reported (Oswald et al., 2013; Su et al., 2011; Wang et al., 2021). These discrepancies are concerning, given recent emphasis from the scientific community on the atmospheric impacts of soil-derived HONO on air quality. Here, the results from our agricultural soil samples may reflect the differences in our methodology, such as the soil handling and preparation steps prior to and during experiments. Many prior reports prepare their samples in ways that strongly deviate from real-world conditions (e.g. initial soil drying temperatures above those occurring under ambient conditions, extreme storage conditions, grinding, sieving, use of dry zero air to flush chambers, etc.). Further drivers of variability within the category of heavily altered samples from the literature include pH, NO_2^- availability, and NH_4^+ or NO_3^- content, all of which are known to influence biotic and abiotic HONO formation pathways (Wu et al., 2019).

Our HONO fluxes from the agricultural soil samples studied here are consistent with field observations under ambient conditions, where average emissions have been reported to largely remain below 2 ng N m^{-2} s^{-1} or 7.2 µg N m^{-2} hr^{-1} (Tang et al., 2019; Xue et al., 2024). This does

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suggest that greater care in sample preparation, and likely also a widely agreed-upon standard procedure, is needed to study soil HONO emissions relevant to atmospheric models.

The integrated HONO fluxes for the pooled replicates yielded 185 µg N m^{-2} and 146 µg N m^{-2}, respectively. From the individual sample replicates, which were slightly wetter than the pooled, the integrated HONO fluxes were 690 and 739 µg N m^{-2}, which was unexpected because the overall moisture regime accessed by the pooled soil experiments was not lower than those from the plot samples. The drier soils would have been expected to yield greater integrated HONO emissions (Oswald et al., 2013), yet this was not the case. Additional replicates and experimental controls, while beyond the scope of this study, would allow further attribution of the controls over the observed HONO variability.

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Table 3. Average and integrated fluxes of NO, NO_2, and HONO (in μg N m^{-2} hr^{-1} and μg N m^{-2}, respectively) from agricultural soil samples across two soil VWC ranges. Both the average and integrated fluxes were calculated over a constant period within the noted range of soil VWC. Values are reported as mean ± standard error.

Soil sample	Soil VWC Range (%)	Duration (hr)	Avg Flux (μg N m^{-2} hr^{-1})			Integrated flux (μg N m^{-2})		
			NO	NO_2	HONO	NO	NO_2	HONO
Pooled R1	16-22	125	1.0 ± 0.04	0.05 ± 0.02	0.06 ± 0.02	2400 ± 120	160 ± 50	190 ± 50
Pooled R2	16-22	125	1.0 ± 0.04	0.20 ± 0.02	0.05 ± 0.01	2500 ± 130	500 ± 60	150 ± 40
Plot R1	22-27	65	1.2 ± 0.05	0.40 ± 0.03	0.20 ± 0.02	3400 ± 150	1300 ± 90	690 ± 70
Plot R2	22-27	65	1.0 ± 0.03	0.50 ± 0.04	0.30 ± 0.02	2600 ± 100	1600 ± 100	740 ± 50

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These findings demonstrate the utility of the modified custom-built dynamic chambers for accurately capturing N_r fluxes under controlled laboratory settings, but they also highlight the need for more such systems to be implemented across the scientific community to better consider both biogeochemical soil properties and environmental context when interpreting the impacts of N_r fluxes obtained in the lab and scaling them to real soils. There seems to be potential for skewing the atmospheric impacts as a result, in particular for HONO, as the standard approaches have been designed to replicate NO fluxes (Behrendt et al., 2014). Most global models do not consider the effect of soil HONO on air quality through O_3 production and oxidation chemistry (Ha et al., 2023). Several modelling studies like Ha et al. (2023) and Tian et al. (2024) have incorporated the order of magnitude or higher HONO fluxes reported from lab studies, like those by Su et al. (2011), Wang et al. (2021), Oswald et al. (2013), and Meusel et al. (2018). They estimated significant HONO production with maximum flux potentials of 830 µg N m^{-2} hr^{-1}, 95 µg N m^{-2} hr^{-1}, 70 µg N m^{-2} hr^{-1}, 55 µg N m^{-2} hr^{-1}, respectively. In contrast, the field observations that do exist suggest that real HONO fluxes are much smaller at 2-17.5 µg N m^{-2} hr^{-1} (Song et al., 2023; Tang et al., 2019). Similarly, Wu et al. (2022) has used the regional WRF-Chem model to explore the impact of soil HONO emissions on the concentrations of atmospheric HONO, OH, and O_3.

Agricultural soil HONO emissions have been suggested to significantly contribute to OH radical production, accounting for approximately 10% to 60% of total OH formation in rural areas before noon (Oswald et al., 2013; Su et al., 2011), which often exceed the contributions from ozone photolysis. Additionally, high HONO emissions from agricultural soils have been reported to increase local O_3 concentrations by ~0.5 - 1.0 ppb in low-NO_x rural environments where VOCs are not limiting (Zhang et al., 2021), with even greater impacts observed during fertilization periods (Wu et al., 2022). Modelling studies, using GEOS-Chem and CMAQ, for example, claim that incorporating soil HONO emissions improves the agreement between observed and simulated O_3 levels, particularly during the morning (Zhang et al., 2021).

Only a few studies have conducted estimates of soil NO_x emissions under reasonable conditions, like Bao et al. (2022) and Wu et al. (2022), where the researchers tried to mimic field conditions. Even in such an area that has been long studied, large uncertainty still exists around soil sources of NO_x, particularly for agricultural activities where uncertainty is still at least ±30% due to limitations in lab characterizations and field experiments (Gong et al., 2025). It is not surprising,

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then, that a similar issue exists for the very recent work on HONO soil emissions. The NO_x uncertainty range results from intricate soil biogeochemical processes and varies with crop types, soil texture, fertilizer types and application rate (Gong et al., 2025). This longstanding and established difficulty in predicting soil NO_x for use in global chemical models means that doing so for HONO without careful ground truthing of real-world emissions could lead to substantial inflation of the impacts on atmospheric chemistry and air quality. Care should be taken in using HONO emissions from lab studies in global models, as it seems they pose a risk of overestimating their atmospheric impacts until a more representative experimental design can be obtained with chamber systems like the one used here.

3.3.2 Fluxes of NH_3, N_2O, NO, NO_2, and HONO from fertilized agricultural soil samples

Agricultural soils amended with chemical fertilizers are expected to be hotspots for NH_3, N_2O, HONO, and NO_x emissions. Here, we demonstrate the use of our developed chambers to measure these analytes under controlled lab conditions using our lightly processed pooled soil samples and four fertilizers: urea, ammonium nitrate (AN), ammonium bicarbonate (ABC), and ammonium carbonate (AC) with the temperature maintained at 23 °C, VWC between 25–29%, and headspace RH held at 65% for three days, simulating realistic atmospheric and environmental N_r flux exchange conditions following farm field fertilization (Figure 3). In all experiments conducted with the Picarro G2509, the mixing ratio of N_2O began to rise approximately four hours after the experiment started. In the example shown for urea, it peaked at 0.79 ppm after 12 hours, which was followed by a gradual decline (Figure 3a). This pattern likely reflects the incubation period of nitrifying and denitrifying bacteria that leads to the subsequent release of gases like HONO, as depicted in Wang et al. (2021), and N_2O in Liu et al. (2022). In contrast, the mixing ratio of NO remained relatively constant throughout the three days (Figure 3b), with NO_2 increasing as the N_2O emissions decreased, while NO was emitted constantly throughout (Figure 3c). In this example experiment, no measurable emissions of HONO were detected despite the substantial presence of urea and evidence of active microbial nitrification and denitrification from the other emitted gases (Figure 3d). Lastly, the urea application example in Figure 3e shows the expected significant NH_3 emissions, with the integrated amount reaching 22% of the applied N over the

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three-day incubation period. These findings are consistent with our existing knowledge that NH_3 volatilization as an N loss mechanism dominates early N_r losses from fertilizers.

Volatilization of NH_3 is well-characterized as a major pathway for N loss from fertilizers (Behera et al., 2013; Govoni Brondi et al., 2024; Liu et al., 2020; Moravek et al., 2019; Pan et al., 2016, 2022; Paulot et al., 2014). Besides agronomic concerns due to N loss and reduced fertilizer efficiency related to NH_3 emissions from fertilized soil (Anas et al., 2020), it is a key precursor to secondary inorganic aerosols in the atmosphere with impacts on respiratory and ecosystem health, visibility, and climate (Dennis et al., 2010; Edwards et al., 2024; Fowler et al., 2013; González Ortiz et al., 2020; Jang et al., 2025; Seinfeld and Pandis, 2006).

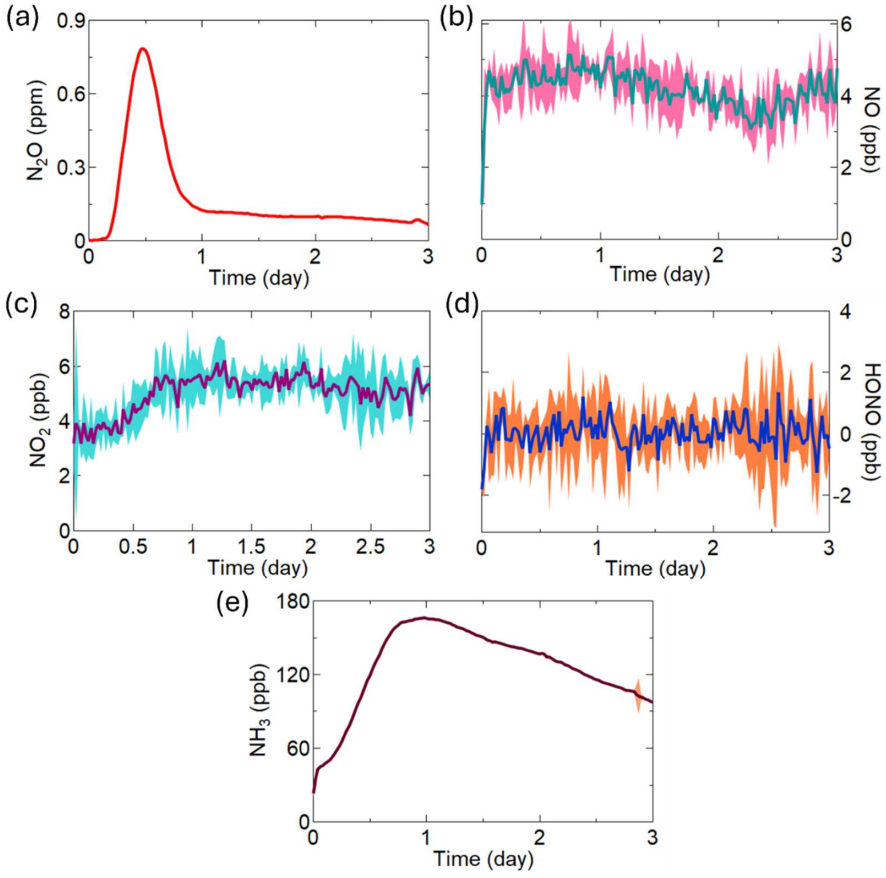

Figure 3. Soil emissions of the comprehensive suite gases from soil treated with urea, including (a) N_2O; (b) NO; (c) NO_2; (d) HONO; and (e) NH_3. The NO, NO_2 and HONO emissions were measured at 1-minute resolution and averaged to 30 min. The standard deviation (±2σ) around these averages is shaded with a lighter version of the main trace colour. Similarly, the 2-second

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resolution of N_2O and NH_3 measurements were also averaged to 30-minute intervals with ±1σ provided in shading.

Emissions of NH_3 and N_2O were observed to be far greater in terms of integrated amounts from the fertilized samples (Figure 4). Integrated flux for NH_3 produced by soil treated with ABC accounted for 77% of total N_r flux (i.e., 85900 μg N m^{-2}), followed by AC, which was 63700 μg N m^{-2}. This is not surprising, since the use of chemical fertilizers increases the concentration of NH_4^+ in the soil that can deprotonate to emit neutral NH_3 and, in the presence of ammonia-oxidizing microorganisms, increases the production of N_2O (Luo et al., 2025). Nitrous oxide released from the addition of urea accounted for the highest integrated flux of 32400 μg N m^{-2} observed, representing 89% of total N_r released, followed by 25300 μg N m^{-2} and 9600 μg N m^{-2} for ABC and AC, respectively. One way that has been proposed to reduce these large N_2O emissions from inorganic fertilizers is to change the application form to organic fertilizer, as the NH_4^+ in soil is released more slowly (Luo et al., 2025). Due to a limited duration of access to the G2509 to conduct this work, we were unable to measure the N_2O and NH_3 emitted from unamended soils or those treated with AN. Regardless, based on the obtained data, the values found here are similar to those observed under real environmental conditions (Figure 4). For our sample without N amendment, the integrated flux of NO was the largest (2400 μg N m^{-2}; 87% of total NO_y), followed by comparable levels of NO_2 (160 μg N m^{-2}) and HONO (190 μg N m^{-2}). The fluxes of NO_x and HONO were below 1 μg N m^{-2} hr^{-1} for all the nutrient addition treatments, suggesting a similar trend as those observed under field conditions and from our lab results with unamended soils (Figure 4, Table S1, Section S6). The exact mechanism behind the HONO release, being due to nitrification and/or denitrification, cannot be definitively assigned based on flux data alone, and many abiotic factors like soil moisture, temperature, and presence of specific microbial communities drive these emissions. There are discrepancies still observed between HONO flux measured from the treated soil samples in the laboratory and similar measurements in literature (Oswald et al., 2013; Su et al., 2011), some of which report fluxes of up to ~3600 μg N m^{-2} hr^{-1} and are likely overestimating the soil N_r fluxes found in the real world. In contrast, our results are in close agreement with the field-based measurements of Tang et al. (2020), which also used a dynamic chamber flux method.

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These in-lab experiments show that simultaneous speciated N_r emissions in a controlled environment can be conducted using a single chamber and potentially applied to an array of chambers, as others have done for a subset of gaseous N_r (Scharko et al., 2015; Tang et al., 2019). With even limited replicates we did here, our results raise a question for researchers who have been using lab studies as a standard to predict and incorporate HONO soil emission values in particular, into regional and global models.

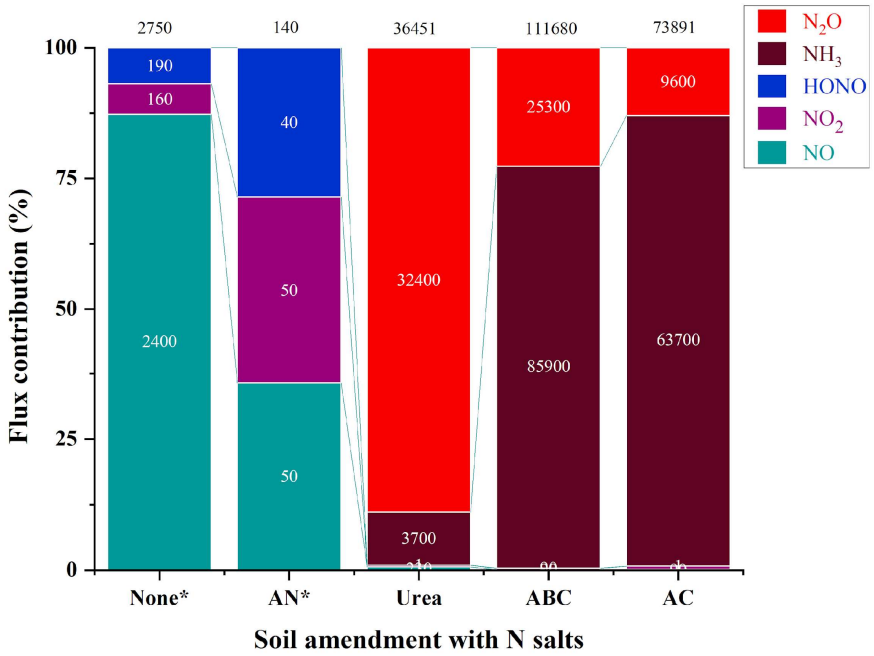

Figure 4. Relative flux contribution of soil treated with four different nitrogen-containing fertilizer salts. Each segment shows the proportion of integrated flux of NO (cyan), NO_2 (purple), HONO (blue), NH_3 (brown) and N_2O (red), with discrete flux values presented in white text, and the total flux provided in black text above the column (µg N m^{-2}). Some samples (denoted by *) were only characterized for fluxes of NO, NO_2 and HONO using the modified NO_x analyzer, as the duration of our access to the G2509 for NH_3 and N_2O measurements was limited.

3.3.3 Dual chamber field deployment for automated continuous dynamic fluxes

A pilot scale field campaign was carried out to demonstrate the application of our dual soil flux chambers in capturing N_r gas exchange processes, taking into account the characterized processes presented above that are necessary for accurate determinations. A paired measurement and reference chamber setup was deployed in the same field a year after the soil samples were collected

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for our lab experiments. During a period of stimulated N_r emission from an experimental application of urea in situ, the mixing ratios of NO, N_2O, and NH_3 were impacted compared to the unfertilized state. The changes within both the measurement and reference chambers were measured and used to calculate fluxes (Figure 5). 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 prior to the fertilization event so that 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. Each set of observations span three consecutive hours of dynamic changes in gas concentrations within the chambers which allow fluxes to be calculated.

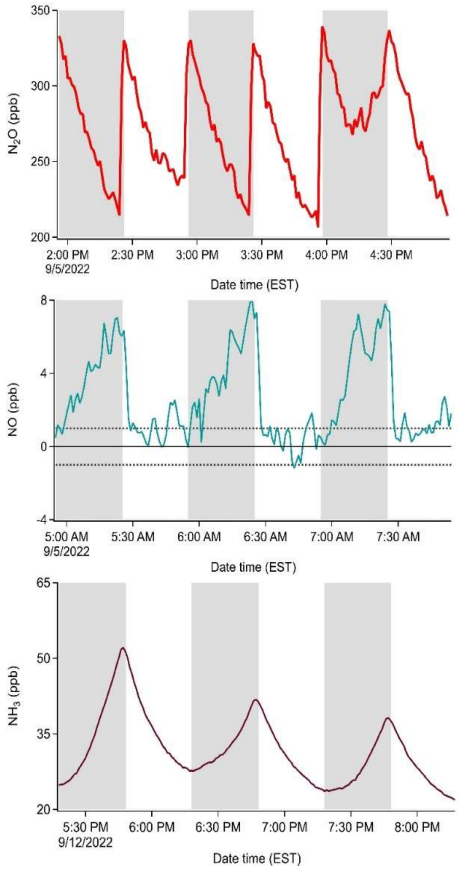

Figure 5. Mixing ratios of N_2O (ppb), NO (ppb), and NH_3 (ppb) in the measurement (grey shading) and reference (unshaded) chambers from three consecutive cycles during the pilot field study. The NH_3 cycles correspond to measurements taken after the fertilization perturbation, while the NO

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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 NO_x analyzer.

The breakdown of the flux components for NH_3, N_2O, and NO can allow the contributions of the experimental setup (e.g. dilution) and environmental factors (e.g. reaction) to be considered independently (Figure 6). We consider these across three consecutive measurement cycles from the pilot field deployment, to provide meaningful examples. The uncertainty in each term is estimated from a triplicate of consecutive reference chamber background measurements. Therefore, the error bars for each term are derived from the variability in the measured slope of the three reference chamber measurements. This error estimate corresponds to that arising only from reference chamber observations used in E6 or E7 and assumes that ambient atmospheric composition did not change substantially during this error derivation period.

The rate term (dC/dt) is the dominant contributor to the determined flux for all three gases (Figure 6), which are all positive and indicate emissions despite their clearly differing temporal trends. Each contribution term is defined and discussed in further detail in Section S7 of the Supplementary Information. Accurate quantification of trace gas fluxes using dynamic chamber systems requires correction for attenuation caused by surface interactions. These effects can significantly suppress the measured accumulation rate of reactive species within the closed chamber, particularly for compounds with notable surface affinities such as NH_3, NO_2, and HONO (Figure 5). To account for such losses, an attenuation factor (λ) was introduced in this work (ES12), defined as the ratio of the theoretical concentration signal to the measured signal over the chamber closure period. The value of λ is gas-specific and time-dependent, reflecting wall affinity and kinetics, which are therefore calculated over the first 30 min of chamber closure, as this was the duration of our field measurement closures. This correction reduces bias that would otherwise result in the calculated gas exchange rates, independent of chamber-specific losses. The highest attenuation was observed for NH_3, for which a λ of 5.40 was determined for the corresponding closure period. That is, substantial bias would result without this correction. Comparative values for NO_2 and HONO are also provided in the Supporting Information (Section S7.3).

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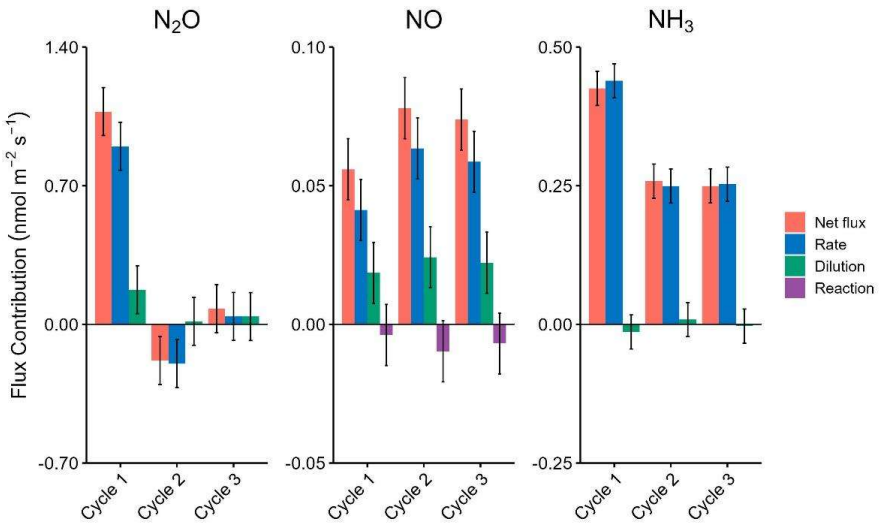

Figure 6. Contributions of different terms (rate, dilution, and reaction) to the net flux of NO, NH_3, and N_2O across three consecutive cycles (nmol m^{-2} s^{-1}). The rate represents the change in concentration measured over time, the dilution represents the integrated loss to dilution, and the reaction represents the contribution of known reactions happening inside the chamber. Error bars are calculated using the mean value of the corresponding terms from three reference chambers plus their standard deviation. For visual clarity, the attenuation correction (λ = 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).

For N_2O, the first cycle exhibits the highest flux (1.07±0.12 nmol m^{-2} s^{-1}), while the second cycle showed uptake by the soil (-0.18±0.12 nmol m^{-2} s^{-1}), and the final cycle showed no net flux within error (0.08±0.12 nmol m^{-2} s^{-1}). This occurs for a non-reactive greenhouse gas like N_2O despite the concentration decreasing with time for both the measurement and reference periods, as the rate of decrease during the measurement cycle is slower than that from dilution alone (Figure 6). Across the three cycles, the rate of concentration change term contributed 84±15% to the measured flux in the first cycle, 109±98% in the second cycle, and 50±171% in the third cycle. The negative rate of change in all of the observation periods arises due to the use of N_2O-free purge gas delivered to the chamber headspace, which is required for the gas sample to be destructively quantified, while not introducing ambient air into the chamber. This simultaneously prevents sudden changes in local outdoor air composition from making small fluxes difficult to detect, as well as reduces the uncertainty in the fluxes assigned. Here, the dilution terms range from 8 to 50% of the net flux, as would be expected from the N_2O exchange switching from emission to deposition during the three-

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cycle example (i.e. 3 hours). In the final measurement cycle, the rate of concentration change transitions from a loss to steady state during the observation period, suggesting that an instant of 'hot spot, hot moment' emission of N_2O was likely occurring. As such, the transition leads to no net flux for the observation period, which is a limitation of our dual-chamber approach compared to one with recirculating headspace, or that of an eddy covariance approach that can capture much higher temporal resolution changes in concentration. 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). Field-scale eddy covariance studies, such as Maier et al. (2022), have captured post-harvest pulses up to 1.6 nmol m^{-2} s^{-1}, highlighting the capacity of EC to resolve large, rapid emission events that single-point chamber systems may miss. However, dynamic chamber systems provide high-precision, temporally resolved flux data under controlled conditions, enabling direct attribution of emissions to specific soil management or environmental factors (Butterbach-Bahl et al., 2013; Kong et al., 2025). This makes dynamic chambers, like those demonstrated here, especially valuable for mechanistic and process-level studies.

For NO, the only gas we consider in the examples here with a reaction term, the reaction contribution is the smallest among the three flux components. Over all three cycles, the reaction term opposed the net flux by less than 13%. The magnitude of the reaction term is always negligible, remaining within the ± 0.01 nmol m^{-2} s^{-1} variability caused by background correction from the reference chamber. Instead, the time rate of change in concentration term drove 74–81% of the total flux for all three cycles and dilution accounted for the remaining 30–33%. The reaction term falling within the uncertainty range of no contribution in all three cycles (e.g. -0.01±0.01 nmol m^{-2} s^{-1} in the second cycle, where it had the greatest potential), indicates that its contribution is less certain than the other flux components as it is driven by the presence of O_3, which is rapidly lost upon chamber closure. Overall, the low contribution of the reaction term suggests this process has a minor role in measured NO fluxes. In other, more polluted regions, such as the North China Plain (NCP) and the Pearl River Delta (PRD), where summertime ambient O_3 concentrations frequently range from 60 to 275 ppbv, and exceedances above 200 ppbv occur during pollution episodes (Wang et al., 2017), this term could become very important to include. As noted above, the PFA film on the chamber surface will change its properties with respect to O_3 transmission

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over time, highlighting the utility of the reference chamber, which is designed to accumulate the same atmospheric compounds as the measurement chamber over time on all sampling surfaces.

The resulting emission fluxes of NO observed in these three cycles were 0.056-0.078 nmol m^{-2} s^{-1}, which is well within the range reported for agricultural soils in North America and Europe, such as Taylor et al. (1999) who observed -0.07-4.2 nmol m^{-2} s^{-1} in Canadian fertilized cropland, and Pape et al. (2009) and Almand-Hunter et al. (2014) who reported values of 0.05-4.0 nmol m^{-2} s^{-1}, using dynamic chambers in grass and cropland soils. Therefore, in the case of NO for this example, the variability in the fluxes is largely driven by real fluctuations in the rate term. This highlights the sensitivity of the total flux to changes in the rate of concentration change, and the precision of the method, as the uncertainty in the final fluxes here is on the order of 14%. Compared to the dynamic chambers reported by these prior studies, our reference chamber in our dual-chamber system offers a clear advantage by directly correcting for baseline fluctuations and environmental drift that can confound single-chamber approaches. This is especially important for reactive gases such as NO, which are susceptible to rapid loss to O_3 and short-term background variability (Taylor et al., 1999). The dual-chamber system provides more robust, artifact-free quantification of soil–atmosphere exchange and is less susceptible to interference from transient local emissions (e.g. from nearby traffic or agricultural equipment) than single-chamber systems. In comparison to eddy covariance or flux-gradient techniques, which integrate over larger areas but may underestimate true NO fluxes due to post-emission chemistry (Taylor et al., 1999; Plake et al., 2015), our approach yields high-frequency, process-resolving data ideal for mechanistic and plot-scale studies.

For NH_3, the rate of change term dominates the total flux, contributing 103 ± 10%, 97 ± 16%, and 101 ± 17% of the flux in cycles one, two, and three, respectively, while the dilution term contributes inconsequentially at -3 ± 7%, 3 ± 12%, and -1 ± 12% in the same three cycles, respectively. The resulting emission fluxes of NH_3 observed across these cycles ranged from 0.43 ± 0.03 nmol m^{-2} s^{-1} in cycle one down to 0.25 ± 0.03 nmol m^{-2} s^{-1} in cycle three. The relatively small contribution of the dilution term is consistent with the expectation that the reference and measurement chambers exhibit similar dilution effects. The relative uncertainty in the final NH_3 fluxes is 7% for cycle one, and 12% for cycles two and three. By comparison, relative uncertainties

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were 14% for NO and ranged from 15% to 171% for N_2O, reflecting the greater variability and lower precision associated with the smaller flux magnitudes for those gases.

Our observed NH_3 fluxes (0.25–0.43 nmol m^{-2} s^{-1}) are consistent with literature values for managed grass and croplands. For instance, Milford et al. (2009) reported bi-directional background fluxes from –3.8 to 2.5 nmol m^{-2} s^{-1} prior to cutting intensively managed grassland, with larger diurnal emissions up to 42 nmol m^{-2} s^{-1} after cutting and maxima up to 224 nmol m^{-2} s^{-1} following fertilizer application. Abdulwahab et al. (2024) observed highly variable fluxes in intensively grazed French grassland, ranging from –6.6 to 188 nmol m^{-2} s^{-1}, with short-lived maxima above 300 nmol m^{-2} s^{-1} after slurry application, though most measurements were at much lower magnitudes. Notably, accurate quantification of NH_3 fluxes in this system critically depends on the application of the chamber-specific attenuation factor λ (Section S.7.3). In our study, λ for NH_3 was 5.40 for the 30-minute closure interval, meaning that without this correction, true NH_3 fluxes would be underestimated by more than fivefold. The necessity of such a large λ correction is due to the strong surface affinity of NH_3 and emphasizes the importance of it for gas- and chamber-specific corrections to obtain high-quality N_r fluxes. While the reference chamber correction plays a role in the flux calculations, its impact on NH_3 is less pronounced than on N_2O, where the correction significantly alters the net flux direction (Figure 5; first cycle). Chamber-based approaches such as ours provide a key advantage for NH_3 over micrometeorological methods like eddy covariance, which are especially prone to high-frequency attenuation and chemical interferences for reactive gases. As shown in Moravek et al. (2019), even state-of-the-art closed-path EC systems may recover less than half (as little as 46%) of true NH_3 fluxes due to instrument limitations and turbulence losses. Challenges were also evident for relaxed eddy accumulation (REA), where Xu et al. (2010) found that turbulence and surface effects complicated flux interpretation in cropland. Related methodological considerations have also been noted in other contexts. Schlossberg et al. (2017) highlighted how airflow and canopy structure can influence chamber NH_3 fluxes in turf systems, underscoring the need for chamber methods that minimize such artifacts. In contrast, our dynamic chamber system, with a chamber-specific λ correction and reference chamber, enables robust, bias-corrected quantification of both low and episodic NH_3 fluxes, as well as clear partitioning of emission and dilution terms, even under highly variable field conditions. Overall, the combination of dual-chamber design with explicit λ correction in our method provides more

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accurate and robust quantification of soil NH_3 emissions than single-chamber, eddy covariance, or relaxed eddy accumulation techniques, particularly for short-term or low-flux events.

4. Conclusions

In this work, we presented a dynamic chamber system for reactive nitrogen flux measurements, developed for the first time through the modification of commercially available chambers by implementing two key changes: the use of PTFE fittings instead of original brass fittings and the installation of an inert PFA film, which retains their actinic transparency. These modifications provide a targeted methodology for other researchers to convert commercially available chambers into those capable of measuring N_r. The performance of these modifications was quantified through the rise and fall time constants of target gas concentrations, as well as a reduction in reactive losses. 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. 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.

Only NO_2 showed reactive loss in the system, and the loss fraction in the chambers in their unmodified configurations was up to ~36%. Losses were reduced to the gas analyzer detection limits (<10%) with the same fluoropolymer modifications when atmospherically relevant NO_2 and RH mixtures were introduced. Lastly, O_3 loss was pervasive within chambers in both their modified and unmodified configurations at 35% and 45% respectively, demonstrating the necessity of the reference chamber. It allows characterization of deposited surface film reactivity for O_3, especially when obtaining quality O_3 measurements is needed to account for the conversion of NO to NO_2 during a sampling period. Taken together, the modified commercial system is capable of measuring dynamic soil fluxes of GHGs and N_r when a measurement and reference chamber are deployed simultaneously.

Proof of concept flux measurements using this N_r dynamic chamber system were conducted using real agricultural soil samples in the lab, with a single chamber, and during a pilot study in the field with a measurement-reference chamber pair. The lab soil emissions were found to be consistent with prior field reports in the literature for NO and HONO, with unexpected emissions of NO_2 also

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observed. Substantial variability in NO_2 and HONO emissions between replicates demonstrates the potential heterogeneity of soil emissions that may result from samples kept intact and subject to minimal preparation conditions. Upon the addition of typical fertilizers, like urea, substantial NH_3 and N_2O emissions fluxes matched expectations, with increasing quantities of NO, NO_2, and HONO as the soil water content decreased.

Last, fully automated operation of the chambers was carried out in a field pilot study with the delivery of external fertilizer conducted at the midpoint of the study to stimulate N_r emissions, mainly in the form of NH_3. Continuous flux observations were made by switching sample flows between a paired reference and measurement chambers with a custom-built valve system to obtain continuous N_r fluxes over two weeks. While the details of the entire campaign will be presented in a future manuscript, it was shown here how the methodology developed yields reliable flux determinations by accounting for known reactions and our lab-derived surface effects. The mathematical foundation of each term and its error in a mass balance equation, which are central to reducing flux bias, are fully described. The observed fluxes from our dynamic chambers are simpler to quantify with standard gas analyzers and can be compared readily with prior reports in the literature from other common flux techniques. One key limitation of the dynamic chamber approach is the limited footprint covered in a system that is notoriously heterogeneous, where EC and REA flux approaches are less prone to this effect. Using a multiplexer and a larger array of dynamic chambers, it is possible to reduce the susceptibility of the dynamic chamber approach to this issue.

Through our modifications and validation, this work provides insight into how commercial dynamic chamber options, like those offered by Eosense, can be modified easily for scientists from various disciplines interested in studying N_r exchange at atmospheric interfaces. This is particularly important for research groups which currently do not have the expertise and resources to develop their own N_r flux measurement systems. The modified system utilizes destructive sampling techniques, as opposed to the re-circulation of chamber air, enabling integration of the dynamic chamber approach with various standard gas analysis instruments (e.g., NO_x chemiluminescence) to study their exchange. The large footprint allows gas concentrations to change in easily determined quantities even for very small fluxes. 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,

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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. Given the pressing need to understand global perturbations to the biogeochemical cycle of N, reduce nitrogen use in agriculture, and gauge the impacts of N status on biodiversity or ecosystem function, wider accessibility of N_r flux techniques for the global research community is needed to increase the pace of research outcomes and improve the capacity for interdisciplinary work between atmospheric and earth system researchers.

Data Availability: Data is available upon request from the Corresponding Author.

Competing Interests: TCV received supporting in-kind funds for this work from Eosense, Inc. and Picarro as it is mandatory in the NSERC Alliance Missions programme funding structure which facilitates research partnerships between the academy and industry. NN, CC, and SE are employed by Eosense, Inc.

Author contributions: TCV designed and oversaw the experiments, acquired funding, wrote parts of the manuscript, and guided writing and revision of all sections of the manuscript. MS wrote the manuscript and performed all the lab experiments. KZA carried out the multiplexer experiments, conducted data analysis for the fill-empty experiment, provided guidance and feedback on the derivation of the mass balance flux model, and assisted in the revision of the manuscript. DF conducted some of the field measurements, worked up the pilot field study results and derived the dual chamber mass balance flux calculations, and made contributions to the writing and revision of the manuscript. LRC helped design the experiments, modify the chambers, write the LabVIEW code, conduct the pilot field measurements, and contributed to manuscript preparation and revision. AM contributed to the initial chamber lab setup and revision of the manuscript. FS performed some fill-empty and NO_2 loss experiments, designed the custom valve switching system, modified LabVIEW code for the pilot field measurements, and contributed to initial drafts of the manuscript. YEI and TH assisted with the GHG fill-empty experiments, YEI supported the pilot field study, and both contributed to manuscript revision. NN, CC, and SE provided technical support with setting up and modifying the chambers and multiplexer.

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