

# Utilizing Novel Field and Data Exploration Methods to Explore Hot Moments in High-Frequency Soil Nitrous Oxide Emissions Data: Opportunities and Challenges

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O'Connell CS, Anthony TL, Mayes MA, Pérez T, Sihi D and Silver WL (2022) Utilizing Novel Field and Data Exploration Methods to Explore Hot Moments in High-Frequency Soil Nitrous Oxide Emissions Data: Opportunities and Challenges. Front. For. Glob. Change 5:674348. doi: 10.3389/ffgc.2022.674348 Soil nitrous oxide (N<sub>2</sub>O) emissions are an important driver of climate change and are a major mechanism of labile nitrogen (N) loss from terrestrial ecosystems. Evidence increasingly suggests that locations on the landscape that experience biogeochemical fluxes disproportionate to the surrounding matrix (hot spots) and time periods that show disproportionately high fluxes relative to the background (hot moments) strongly influence landscape-scale soil N<sub>2</sub>O emissions. However, substantial uncertainties remain regarding how to measure and model where and when these extreme soil  $N_2O$ fluxes occur. High-frequency datasets of soil N2O fluxes are newly possible due to advancements in field-ready instrumentation that uses cavity ring-down spectroscopy (CRDS). Here, we outline the opportunities and challenges that are provided by the deployment of this field-based instrumentation and the collection of high-frequency soil N<sub>2</sub>O flux datasets. While there are substantial challenges associated with automated CRDS systems, there are also opportunities to utilize these near-continuous data to constrain our understanding of dynamics of the terrestrial N cycle across space and time. Finally, we propose future research directions exploring the influence of hot moments of N2O emissions on the N cycle, particularly considering the gaps surrounding how global change forces are likely to alter N dynamics in the future.

Keywords: soil nitrous oxide emissions, novel methods, high-frequency data, hot spots and hot moments, nitrogen cycling, soil greenhouse gas

# INTRODUCTION

Globally, soils are the largest source of nitrous oxide (N<sub>2</sub>O) to the atmosphere (Tian et al., 2020) and soil N<sub>2</sub>O emissions have substantial influence over both the nitrogen (N) cycle and landscape-level greenhouse gas (GHG) emissions (Groffman et al., 2009). Fluxes of N<sub>2</sub>O at the soil-atmosphere boundary tend to be episodic in nature due to short-lived peak emissions (a.k.a., "hot moments") resulting from pulse events associated with natural (e.g., storm events, freeze-thaw cycles) and

anthropogenic (e.g., fertilization in agricultural soils, flood irrigation) factors (Molodovskaya et al., 2012; Wagner-Riddle et al., 2017, 2020). Additionally, a small proportion of landscape locations can be predisposed to biogeochemical fluxes disproportionate to the surrounding matrix (a.k.a., "hot spots"), also as a result of natural (e.g., hydrologic, redox dynamics, aggregate microsites) and anthropogenic factors (e.g., landscape management decisions) (Silver et al., 1999; Groffman et al., 2009; Bernhardt et al., 2017; Barcellos et al., 2018).

Measurements at discrete time points (e.g., bi-weekly or monthly) or with limited replication across a landscape in traditional field campaigns can miss these critical hot spots and hot moments. Missing these hot moments or under-observing hot spots can result in large uncertainties in national and global inventories (Tian et al., 2020). To that end, researchers have attempted to identify optimum sampling frequency (daily to weekly) or time (e.g., mid-morning to mid-day, late evening) that can increase precision and reduce disparities in terrestrial N<sub>2</sub>O budget estimates (Smith and Dobbie, 2001; Parkin, 2008; Barton et al., 2015; Reeves and Wang, 2015). However, there remain open questions about how best to measure, model and predict hot spots and hot moments of soil N2O fluxes. It is therefore imperative that we develop both robust methodologies for observing patterns of hot spots and hot moments of soil N2O emissions and, at the same time, models that can aid in predicting and scaling them.

Over the past decade, several optical techniques, including cavity ring-down spectroscopy (CRDS), have been developed and deployed in the field (Figure 1) to measure ecosystem trace gas fluxes (Rapson and Dacres, 2014). The major advantage of these techniques is their ability to carry out high frequency measurements of a number of trace gases simultaneously. With CRDS, spectra can be obtained roughly every 2 s (Christiansen et al., 2015), generating 15-30 times more data points per flux measurement than traditional "manual" chamber-based flux measurements. The simultaneous development of automated chambers, which allow for continuous and unmonitored operation via chamber-management software (such as EosAnalyze-AC, Eosense, Nova Scotia, Canada or SoilFluxPro, LI-COR Biosciences, Nebraska, United States), has created the ability to conduct pseudo-continuous in situ flux measurements capable of five or more individual N2O flux measurements per hour (Diefenderfer et al., 2018; Hemes et al., 2019). Other recent technologies utilized in ecosystem-scale applications include continuous wave quantum cascade laser (QCL) N<sub>2</sub>O gas analyzers (Savage et al., 2014; Cowan et al., 2020), eddy covariance (Tallec et al., 2019), and flux gradient (Wagner-Riddle et al., 2017) methods. Among these techniques, CRDS systems combined with automatic soil chambers provide the ability to capture the spatial and temporal heterogeneity of N<sub>2</sub>O fluxes at the plot scale needed to better constrain N cycle processes and controls.

The emergence of field-ready, automated GHG instrumentation that can measure soil  $N_2O$  emissions has made studying hot spots and hot moments of soil  $N_2O$  fluxes more tractable. However, there remain numerous challenges to implementing these systems in the field, as well as challenges

associated with analyzing these new high-frequency datasets and incorporating these findings into process-based ecosystem and Earth system models. High-frequency data on soil  $N_2O$ emissions is quickly becoming available as more automated CRDS systems are deployed. Here, we outline challenges and opportunities associated with novel field and data exploration methods that explore the hot moments present in high-frequency soil  $N_2O$  data. We discuss the advantages, disadvantages and applications of automated CRDS flux systems. We additionally outline strategies for analyzing and scaling high-frequency soil  $N_2O$  emissions data. Finally, we suggest areas for future research that leverage these emerging methods and experimental design paradigms to improve our understanding of N cycle processes and regional or global  $N_2O$  budgets.

# FIELD INSTRUMENTATION: CAVITY RING-DOWN SPECTROSCOPY FOR ECOSYSTEM SCIENCE APPLICATIONS

# Pioneer Research Advancement on Automated Chambers for Greenhouse Gas Flux Measurements

The first automated system for measuring GHG fluxes was designed by Silvola et al. (1992). This method consisted of six chambers with pneumatic open and close valves. When GHG fluxes were measured, the selected chamber closed, a pump circulated air through the chamber and to a mobile lab located 50 meters away. An aliquot of the chamber air was injected into a gas chromatograph (GC) at 5-min intervals for the 20 min of chamber closure. The GC included thermal conductivity, electron capture and flame ionization detectors for measuring CO<sub>2</sub>, N<sub>2</sub>O and CH<sub>4</sub> concentrations, respectively. Also during that time, flux gradient measurements by Fourier Transform Infrared spectroscopy (FTIR) showed that CO<sub>2</sub>, N<sub>2</sub>O and CH<sub>4</sub> could be measured at large scale from agricultural land (Griffith and Galle, 2000). The increased frequency of measurements obtained by pioneer automated chamber research (Table 1) allowed the capture of diurnal variations and enhanced both our understanding of microbial processes responsible for soil GHG fluxes and the physicochemical variables related to them.

# Advantages and Disadvantages of Automated and Manual Chamber Systems

The deployment of automated chambers using fast response spectroscopic methods (i.e., CRDS, FTIR, among others) further increases the potential frequency of soil GHG fluxes. These methods also have a number of advantages over manual GC flux measurements (Christiansen et al., 2015; Brannon et al., 2016; Lebegue et al., 2016; Keane et al., 2018; O'Connell et al., 2018; Barba et al., 2019; Courtois et al., 2019; Anthony and Silver, 2021). Current CRDS automated chamber system flux measurement time is about 10 min, at least a third shorter than previous automated chamber systems (**Table 1**). Additionally, manual chambers are highly labor intensive, limiting the number of



FIGURE 1 | (A) Sampling configuration for continuous soil GHG emissions by CRDS and applicable soil physicochemical variables (in this case, e.g., soil moisture, temperature, and oxygen sensors). A circulating pump draws air after chamber enclosure. The air passes through a multiplexer where is directed to the CRDS for pseudo-continuous GHG concentration measurements. (B–F) Field deployment of automated CRDS systems including in tropical high-rainfall ecosystem [Luquillo Experimental Forest, Puerto Rico (C)], in flooded soils [California, United States (B,D)] and agricultural systems [California, United States (E,F)].

TABLE 1   Pioneer methods for automated	d greenhouse gas flux measurements.
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Method	Greenhouse gas	Number of chambers	Flux measurement time (min)	References
Gas chromatography	CH4, CO2, N2O	6	48	Silvola et al., 1992
Gas chromatography	N <sub>2</sub> O	8	35	Crill et al., 2000
Gas chromatography	CH <sub>4</sub> , N <sub>2</sub> O	5	24	Butterbach-Bahl et al., 1998
Gas chromatography	N <sub>2</sub> O	6	30	Akiyama et al., 2000
Non-dispersive infrared spectroscopy	CO <sub>2</sub>	10	18	Goulden and Crill, 1997
Non-dispersive infrared spectroscopy, gas chromatography	CH <sub>4</sub> , CO <sub>2</sub> , N <sub>2</sub> O	6	30	Nishimura et al., 2005
Fourier transform infrared spectroscopy	CH4, CO2, N2O	N/A	N/A	Griffith and Galle, 2000*

\*Flux-gradient technique.

individual flux measurements possible (Pattey et al., 2007; Görres et al., 2016), and they have much lower temporal sensitivity given the significantly longer sampling times required (>30 min/flux). This infrequent sampling also has the potential to overlook event-based, diurnal and day-to-day variability (Reeves et al., 2016). Many manual chamber flux measurements are taken weekly or monthly (Teh et al., 2011; Matson et al., 2017; Krichels and Yang, 2019); infrequent measurements can miss or underestimate hot moments of N<sub>2</sub>O flux (Barton et al., 2015; Reeves et al., 2016).

However, manual chamber measurements also have a number of advantages in comparison to automated chamber systems. These include the ability for widespread deployment across soil conditions and simpler deployment in remote ecosystems. They also have the ability to sample a large spatial area over a short period of time and have comparatively low analyzer costs (one central GC for subsequent sample analysis vs. an individual CRDS analyzer needed per field site) (Pattey et al., 2007; Rapson and Dacres, 2014; Görres et al., 2016; Grace et al., 2020). Additionally, to overcome the underestimations related to hot moments of  $N_2O$  flux, strategic sampling integrating process modeling and statistical methods can substantially improve cumulative flux estimation accuracy using infrequent chamberbased methods (Saha et al., 2017).

The most important advantage of CRDS analyzers is the combination of high precision, resulting in a lower minimum detectable flux, with high measurement frequency, that allows for real-time flux determination. In conjunction with automated chambers, CRDS analyzers can continuously measure fluxes at a relatively high temporal frequency (Rapson and Dacres, 2014; Harris et al., 2020). Increasing the number of flux measurements enables capture of short-term N<sub>2</sub>O pulses, which can generate the bulk of environmentally relevant net N2O emissions to the atmosphere (Butterbach-Bahl et al., 2013; Savage et al., 2014). Automation also provides the ability to more accurately determine the magnitude and duration of N<sub>2</sub>O fluxes following N fertilization, irrigation, or other environmental disturbances (Grace et al., 2020). This is particularly important in ecosystems where manual chambers would be difficult to access or cause soil disturbances, which can be an issue with repeated manual sampling events during hot moments of significant N<sub>2</sub>O flux, including flooding or freeze-thaw events.

Further advancements in CRDS technology have also allowed for the measurement of stable isotope ratios and site preference

in N<sub>2</sub>O molecules (Yoshida and Toyoda, 2000; Harris et al., 2020). Isotopic N<sub>2</sub>O and site-preference measurements can provide important information about the environmental sources of N<sub>2</sub>O production (e.g., nitrification vs. denitrification, soil N sources) (Decock and Six, 2013; Heil et al., 2014; Winther et al., 2018). With CRDS analyzers, these measurements can now be performed *in situ*, as some of these instruments can analyze the N<sub>2</sub>O isotopic composition in gaseous mixtures, providing real-time data with minimal sample pretreatment. These measurements can be used to better resolve the drivers of N<sub>2</sub>O production and consumption, previously impossible with non-optical measurement techniques.

The largest disadvantage of automated CRDS systems is the need for a stable, continuous power supply and the system's significant energy demand (~1 kWh), although energy-efficient portable CRDS analyzers have been developed to measure other trace gases (Jeffrey et al., 2019; Brachmann et al., 2020). This electrical demand limits the ability to continuously deploy these systems in remote locations. Generators or solar power have been used with CRDS in remote locations (e.g., savannah woodlands and tropical rainforests; Livesley et al., 2011; O'Connell et al., 2018; Courtois et al., 2019), but continuous deployment involves significant labor and/or travel costs needed to maintain instrumentation functionality. Deployment of CRDS technology is also hindered by instrumentation costs (systems are generally greater than \$85k USD), equipment sensitivity to environmental conditions (e.g., high temperatures or humidity), and the difficulty of automated chamber deployment in complex, heterogenous field environments (Reeves et al., 2016; Grace et al., 2020). Additionally, the deployment of automated CRDS systems can be challenging when spectral interferences with other atmospheric constituents, particularly H2O, occur (Harris et al., 2020). Such interferences increase the challenges CRDS systems face in further constraining measurements of the soil N cycle (Kim et al., 2012), but can also be minimized with installation of in-line water traps (Erler et al., 2015; Murray et al., 2018; Figure 1).

Some of the other disadvantages to automated systems can be overcome by the simultaneous utilization of manual chamber measurements (Savage and Davidson, 2003). Manual chambers can help increase the extent of sampling across space during important flux measurement periods, increasing the ability to detect spatiotemporal variability. This combination can also

Opportunities Using High-Frequency N2O Data

be a useful approach in experiments where it is necessary to compare a large number of treatments, because the number of automated chambers per CRDS system is limited (Savage et al., 2014; Grace et al., 2020). To aid future experimental design, we provide a potential road map for the selection of appropriate methods. Manual chambers are recommended when budget, large number of treatments, remoteness, and access of land power are a constraint. If these constraints are overcome, automated chambers with spectroscopic methods are advisable. To capture hot spots of N<sub>2</sub>O emissions it may be necessary to combine manual measurements with an automated chamber system (Savage and Davidson, 2003). We recommend that automated chambers be placed in locations that are likely to capture hot moments of emissions (e.g., areas with fluctuating redox, high plant activity, or where fertilizer is applied heavily) with a similar number of automated chambers being placed in areas not expected to be predisposed to hot moments, in order to avoid biasing the overall dataset. Manual chambers, in contrast, could be used in likely hot spots (e.g., low lying areas and areas with soil compaction, poor diffusion or slow water infiltration) with, again, a similar number placed in areas suspected to not be hot spots. Further, it is common for automatic chambers to be deployed and remain in a fixed location throughout a field campaign, which can lead to bias in which micro-scale abiotic conditions are favored within a dataset. When field access is not limited, one solution to this potential bias would be to relocate automated stationary chambers at periodic intervals, though that comes with the disadvantage of losing data continuity in a given chamber location. We recommend a priori decisions about how often and where to move chambers (e.g., to a random set of subplot quadrats, seasonally, or quarterly) so as to avoid inserting bias toward within the captured data (e.g., by moving a chamber after a hot spot appears to "resolve" and thus skewing emissions data upwards).

# Applications of Automated Cavity Ring-Down Spectroscopy Flux Systems

In general, the high temporal frequency of automated measurements greatly improves the ability to measure (and predict) the effects of soil management decisions or other environmentally relevant events. The increasing availability of automated CRDS systems has allowed for measurement of N2O fluxes and the ability to capture hot moments in mangrove forests (Murray et al., 2018), tropical rainforests (Courtois et al., 2019), desert (Eberwein et al., 2020), and during freeze-thaw cycles (Ruan and Robertson, 2016; Wagner-Riddle et al., 2017), drought events (O'Connell et al., 2018), soil rewetting events (Liang et al., 2016; Hemes et al., 2019; Liu et al., 2019), and fertilization application in agroecosystems (Savage et al., 2014; Cowan et al., 2020). Increased application of automated flux measurements using CRDS instrumentation may also increase observations of other short-term (hourly to multi-day) hot moments previously undetected from less frequent flux measurement techniques, including for other GHGs. For instance, correlation on hourly scales between soil temperature/moisture and GHG fluxes could constrain microbial mechanisms of soil GHG production, with

implications for ecosystem-level estimates (i.e., Martin et al., 2012). Net ecosystem exchange (NEE) is affected by seasonal variability in plant activity (e.g., variability in root respiration and exudate production) (Curiel Yuste et al., 2007). Forest canopy photosynthesis affects ecosystem respiration but the timing of links between canopy photosynthesis and ecosystem respiration is not well understood (Mencuccini and Hölttä, 2010). In these two examples, high frequency soil CO<sub>2</sub> fluxes could aid in accounting for the relative contribution of soil GHG fluxes to NEE. Future deployments of high-frequency systems, in combination with continuous ecosystem-scale eddy covariance flux measurements (Wagner-Riddle et al., 2017), may further constrain the specific importance of hot spots and/or hot moments on net ecosystem  $N_2O$  (and other GHG) fluxes.

# DATA APPLICATIONS: LEVERAGING HIGH-FREQUENCY SOIL N<sub>2</sub>O EMISSIONS DATA

## **Constraining N Cycle Uncertainties**

High-frequency soil  $N_2O$  datasets require different data management strategies than those designed for traditional manual chamber experimental designs, due to both the large size of these datasets and the structure of the time-series data itself. Numerical modeling approaches have been developed to improve the precision of measured soil GHG fluxes in automated CRDS systems (Creelman et al., 2013). Increased precision combined with the improved temporal coverage of high-frequency data can substantially improve our understanding of N-cycling processes and budgets.

Year-round measurements of high-frequency N<sub>2</sub>O emissions can improve gap-filling methods by accounting for concurrent changes in multiple covariates (Dorich et al., 2020). For example, a recent study demonstrated that ignoring winter emissions from croplands subjected to freeze-thaw cycles can significantly underestimate global agricultural emissions (Wagner-Riddle et al., 2017). The use of a near-continuous flux gradient method, made possible by using a tunable-diode-laser (TDL) trace gas analyzer (Grace et al., 2020), was central to this finding: N<sub>2</sub>O data collection during winter using manual chambers was previously impractical or would highly perturb soil conditions. Edge season emissions associated with microbial decomposition of crop residues in intensive agricultural systems can also increase agricultural N<sub>2</sub>O emission (Scheer et al., 2017). During the growing season, fertilizer-derived N2O emissions can increase exponentially instead of the generally assumed linear functions conventionally used in the Intergovernmental Panel on Climate Change reports (Shcherbak et al., 2014; Gerber et al., 2016). Accurately accounting for these agricultural N<sub>2</sub>O emissions using high-frequency data can help close the global N budget and guide mitigation strategies (Mosier et al., 1998; Syakila and Kroeze, 2011).

High-precision pseudo-continuous measurement technologies also improve confidence in field measurements that observe net consumption of atmospheric N<sub>2</sub>O in soils. These observations, which have been seen in soils ranging from poorly drained wetlands to well-drained upland soils, could, in traditional methods, be discarded as measurement error or experimental noise (Chapuis-Lardy et al., 2007; Eugster et al., 2007; Goldberg and Gebauer, 2009; Schlesinger, 2013; Savage et al., 2014). The occurrence of net N<sub>2</sub>O reduction in well-drained soils warrants an improved understanding of spatial heterogeneity of anaerobic microsites where N2O can get reduced to N2 via biological denitrification (Parkin, 1987). Representation of spatial heterogeneity is crucial for upscaling mechanistic processes related to N2O production and consumption occurring at the aggregate scale to landscape, regional, and global scales (Ebrahimi and Or, 2018; Sihi et al., 2019). Mechanistic representations in process-based landsurface models of varying complexity (Tian et al., 2018, 2020), an alternative of statistical extrapolation of field measurements, is a widely used bottom-up approach to quantify global N2O sources and sinks, which also rely on the availability and quality of open-source data.

# **Big Data Approaches and Model** Integration

Several statistical strategies have been successful at integrating high-frequency soil N2O datasets into investigations at the regional, continental or global scales. The use of simple statistical models has led to contrasting and disparate national and global N2O budgets (Gerber et al., 2016). In contrast, Bayesian Markov Chain Monte Carlo algorithms offer the potential to unravel multiple confounding factors and improve predictions of high-frequency soil N2O fluxes by process-based biogeochemical models (Myrgiotis et al., 2018; Sihi et al., 2019). Alternatively, process-based models coupled with machinelearning approaches can be used to evaluate N2O dynamics and driver-response relationships in long-term high-frequency N<sub>2</sub>O data (Saha et al., 2021). Inequality indicators (e.g., Lorenz curve and Gini coefficient) have also been used to assess hot or cold spots or moments in soil N2O fluxes from highfrequency data collected from heterogeneous landscapes (Saha et al., 2018). Statistical methods used for hot-moment analysis of other time-series soil flux data, i.e., wavelet analysis, can also be used for identifying hot-moments in soil N2O fluxes (Liptzin et al., 2010; Vargas et al., 2018). These strategies have different computational demands, need differing levels and types of input data, operate either within or independently from process-based modeling frameworks, and have different levels of predictive power; determining the appropriate statistical approach for a given application can include assessing the quality of input data and considering the tractability of various statistical methods (Figure 2).

The Global N<sub>2</sub>O Database (Dorich et al., 2020)<sup>1</sup> holds promise to lower uncertainty in annual N<sub>2</sub>O estimates. It provides ample opportunities for future analysis and in-depth comparisons among different methods, crop types, and management practices (e.g., irrigation, tillage). Harmonization with other highfrequency open-source soil flux data like COntinuous SOil REspiration (COSORE; Bond Lamberty et al., 2020) data and collaboration with well-established ecosystem flux communities like AmeriFlux<sup>2</sup> and FluxNet<sup>3</sup> can potentially increase the user pool of the Global N<sub>2</sub>O Database and improve the flux processing pipelines and gap-filling algorithms. Institutional back-up, builtin analytical and statistical tools, availability of analysis scripts using open-source software, and an interactive web interface further encourage researchers to conduct advanced statistical analysis with long-term, high-frequency N<sub>2</sub>O data.

# **FUTURE DIRECTIONS**

# **Rethinking Nitrogen Cycle Processes and Budgets**

Hot spots and hot moments of soil N2O emissions can account for large proportions of total ecosystem N2O flux, with the proportion varying widely across systems and contexts (Groffman et al., 2009; Turner et al., 2016; Bernhardt et al., 2017). CRDS systems can be deployed alongside high-frequency sensors that measure abiotic soil variables [e.g., soil moisture, temperature and oxygen (O<sub>2</sub>), Figure 1]. Such designs can quantify the importance of soil N2O hot moments and what abiotic conditions correlate with those fluxes: in a Northern California grassland system, > 80% of the emitted N<sub>2</sub>O occurs during "hot moments" (Anthony and Silver, 2021). These studies thus far are uncommon, geographically biased, and not always conducted in biomes and regions shown to be globally important sources of N2O emissions (Bond Lamberty et al., 2020; Dorich et al., 2020). There is a critical need to deploy automated CRDS systems under more field conditions and across ecosystems to better quantify the importance of hot moments within the N cycle.

Measuring high N2O flux events in situ provides an excellent template to explore the molecular and microbial dynamics of N<sub>2</sub>O production and consumption in soils. With the proliferation of high-frequency soil N2O emissions data, laboratory incubation experiments (using natural abundance stable isotopes or <sup>13</sup>C or <sup>15</sup>N labeled substrates) would allow us to better understand the microbial processes associated with these high fluxes (Kuzyakov and Blagodatskaya, 2015). For example, pool dilution techniques allow for the determination of gross rates of N2O production and consumption under simulated field conditions (Yang et al., 2012) which would help produce better estimates of denitrification-derived N2 fluxes to the atmosphere. Tools from microbial ecology and bioinformatics may also be able to improve experimental design and guide the deployment of automated chambers (Kuzyakov and Blagodatskaya, 2015). Finally, metagenomic and other high-resolution techniques can be useful to identify microbial functional types associated with the spatial or temporal configuration of N<sub>2</sub>O fluxes.

This work is especially critical in agricultural systems. Anthropogenic global  $N_2O$  sources related to fertilizer applications are responsible for 30% of the tropospheric

<sup>&</sup>lt;sup>1</sup>https://ecoapps.nrel.colostate.edu/global\_n2o/

<sup>&</sup>lt;sup>2</sup>https://ameriflux.lbl.gov

<sup>&</sup>lt;sup>3</sup>https://fluxnet.org



N<sub>2</sub>O concentration increase in the past 4 decades (Tian et al., 2020). Measurements of the isotopic composition of N<sub>2</sub>O in the global atmosphere combined with knowledge of the "isotopic fingerprints" of N<sub>2</sub>O sources (e.g., soils, freshwater, and oceans) and sinks (e.g., stratospheric photolysis and photooxidation) have been used in both "bottom up" and "top down" approaches to explain the current increase in global tropospheric N2O concentrations (Pérez et al., 2001; Park et al., 2012; Snider et al., 2015; Prokopiou et al., 2018). Changes over time show increased atmospheric N2O is largely due to increased fertilizer use in agriculture, as expected (Pérez et al., 2001; Park et al., 2012; Prokopiou et al., 2018). Continuous CRDS measurements of N<sub>2</sub>O isotopic composition from agricultural systems can capture the N<sub>2</sub>O isotopic fingerprint of high flux events, which can constrain the relative contribution of fertilizer-derived N2O from background emissions rates.

# Pairing High-Frequency Data Collection With Modeling Approaches

Numerous opportunities exist to improve input data for models. High-frequency soil N<sub>2</sub>O flux data can be used to better validate modeled GHG fluxes predictions from natural or agricultural systems. Available models (e.g., Daycent, DNDC, and EPIC) often use static chamber soil GHG measurements as validation data, which can lead to underestimation of landscape N<sub>2</sub>O fluxes, likely due to an underestimation of the magnitude of peak daily fluxes (Gaillard et al., 2018). High-frequency data with better estimates of peak daily fluxes can improve estimates of N<sub>2</sub>O emissions; improved N<sub>2</sub>O emissions data can also improve the underlying statistical relationships upon which these models rely (Bond Lamberty et al., 2020; Dorich et al., 2020).

Recent advances in machine learning (ML) models for predicting  $N_2O$  soil fluxes have been shown to improve

outputs derived from process-based modeling (Saha et al., 2021). However, when comparing classical regression, shallow learning, and deep learning ML model performances, only the heavy computational deep neural network Long Short-Term Memory (LSTP) model is successful in predicting N<sub>2</sub>O fluxes from agriculture using a static chamber data time series as the input (Hamrani et al., 2020). The low performance of the other ML algorithms could be related to the intrinsic characteristic of the method. As an example, random forest machine learning applied to a dataset that had both automated chambers and continuous measurements of soil volumetric content gave the same generalized validation ( $R^2 = 0.38$ ) (Saha et al., 2021) as one obtained by other studies that had both static chamber N2O fluxes and discrete soil physicochemical measurements (R<sup>2</sup> values between 0.37 and 0.39, Hamrani et al., 2020; Glenn et al., 2021). Therefore, to better assess N2O flux prediction robustness of available models (ML algorithms, statistical, process-based and Bayesian modeling approaches), high frequency data of both N2O fluxes and measured variables (physicochemical, micro and macro-meteorological, spectral, etc.) would be required. This could be more achievable as new high frequency technology for measuring physicochemical variables such as pH, NH4<sup>+</sup> and  $NO_3^-$  become available (Figure 2).

High frequency measurements of driving variables are needed as inputs to ML models. Moisture, temperature, and O<sub>2</sub> sensors with sufficient capacity are widely available and have been used in a large number of studies (i.e., O'Connell et al., 2018;Anthony and Silver, 2021). The high cost of environmental sensors currently limits their widespread adoption and use. CRDS systems typically cost over \$85k USD and automated chambers can be  $\sim$ \$3– 10k USD each depending on their features. Soil sensors (e.g., O<sub>2</sub>, moisture, temperature) also tend to be costly, often several hundred dollars per sensor with high spatial replication needed to capture plot-scale variability. New printable sensor technology has the potential to make advances not only in the variables mentioned above, but also in measurements of inorganic nitrogen species (i.e., substrates for  $N_2O$  production in nitrification and denitrification processes). They have the potential to drastically lower costs and increase replication in the future (Sui et al., 2021).

Broadly, increasing the accuracy, precision and temporal coverage of soil  $N_2O$  flux estimates along with other relevant variables across time and ecosystems will be crucial for scaling observational work and incorporating climate feedbacks into global models. Global change will likely alter soil  $N_2O$  emissions in intersectional ways, both as climate and agricultural management change (Griffis et al., 2017). Novel field and data exploration methods that can better observe hot moments of soil  $N_2O$  flux can be leveraged to constrain our understanding of the N cycle as well as improve our ability to predict landscape-level GHG feedbacks under global change conditions.

## CONCLUSION

Utilizing novel field and data exploration methods to explore hot spots and especially hot moments in high-frequency soil GHG data has the potential to transform our ability to measure, analyze and predict patterns of soil greenhouse gas, and especially  $N_2O$ , emissions from terrestrial ecosystems. While there are currently substantial challenges involved, this technology is rapidly evolving. Future research should seek to further constrain our understanding of N cycling dynamics *via* high-frequency data collection across ecosystem type, region, disturbance regime, and under global change scenarios. These efforts are crucial to test and validate ecosystem modeling approaches, to improve the geographic representation of field-based datasets of soil  $N_2O$ emissions, and to enhance our understanding of the processes and patterns that underlie the terrestrial N cycle.

# **AUTHOR CONTRIBUTIONS**

All authors listed have made a substantial, direct, and intellectual contribution to this work as well as contributed to the writing of the manuscript.

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