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

Keywords

Soil nitrous oxide emissions, Novel methods, High-frequency data, hot spots and hot moments, Nitrogen Cycling, Soil greenhouse gas

Abstract

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Soil nitrous oxide (N2O) 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 N2O emissions. However, substantial uncertainties remain regarding how to measure, model and predict where and when these extreme soil N2O 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 N2O 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.

Contribution to the field

Michelle Y. Wong Postdoctoral Researcher Cary Institute of Ecosystem Studies Feb. 28, 2021 Dear Dr. Wong, We are pleased to submit a Mini-Review format manuscript entitled “Utilizing novel field and data exploration methods to explore hot moments in high-frequency soil nitrous oxide emissions data: Opportunities and challenges” to be considered for publication as a part of the “New Frontiers and Paradigms in Terrestrial Nitrogen Cycling” Research Topic. Soil nitrous oxide (N2O) emissions are an important driver of climate change and are a major mechanism of nitrogen (N) loss from terrestrial ecosystems. “Hot spots” and “hot moments” of N2O emissions from soil strongly influence landscape-scale soil N2O emissions, but substantial uncertainties remain regarding how to measure, model and predict these extreme soil N2O fluxes. However, over the past decade several optical techniques, including cavity ring-down spectroscopy (CRDS), have made it newly possible to collect high-frequency datasets of soil N2O fluxes. These systems and their data streams are rapidly improving our understanding of a crucial N loss pathway. Our paper outlines the opportunities and challenges that are provided by the deployment of automated CRDS systems. There are substantial opportunities to utilize the near-continuous data from these set ups to constrain our understanding of dynamics of the terrestrial N cycle across space and time. Additionally, we propose future research directions that capitalize on these instrumentation and data advancements. We believe that this contribution is the first that succinctly summarizes and collates the opportunities and challenges associated with the high-frequency soil N2O data that is increasingly being collected across a range of ecosystems and ecological conditions. This mini-review would be of interest not only to field-focused biogeochemists, but also to ecosystem modelers and scientists interested in open and distributed data. Further, we believe that it contributes directly to the theme of this special issue, as it “highlight[s] new approaches to overcoming perennial challenges in studying soil nitrogen cycling.” We declare that this manuscript is original, has not been published before and is not currently being considered for publication elsewhere. There are no known conflicts of interest associated with this publication and the manuscript has been read and approved by all named authors. Thank you for your consideration and we look forward to hearing from you. Sincerely, Dr. Christine S. O’Connell on behalf of the authorship team

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Utilizing novel field and data exploration methods to explore hot moments in high-frequency soil nitrous oxide emissions data: Opportunities and challenges

Running Title (max 5 words):

Opportunities using high-frequency N_2O data

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Abstract

Soil nitrous oxide (N_2O) 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_2O 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 N_2O 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_2O 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 N_2O emissions on the N cycle, particularly considering the gaps surrounding how global change forces are likely to alter N dynamics in the future.

Introduction

Globally, soils are the largest source of nitrous oxide (N_2O) to the atmosphere (Tian *et al.* 2020) and soil N_2O emissions have substantial influence over both the nitrogen (N) cycle and landscape-level greenhouse gas (GHG) emissions (Groffman *et al.* 2009). Fluxes of N_2O 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_2O budget estimates (Smith and Dobbie 2001; Parkin 2008; Reeves and Wang 2015; Barton *et al.* 2015). However, there remain open questions about how best to measure, model and predict hot spots and hot moments of soil N_2O fluxes. It is therefore imperative that we develop both robust methodologies for observing patterns of hot spots and hot moments of soil N_2O 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 two seconds (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, USA), has created the ability to conduct pseudo-continuous *in-situ* flux measurements capable of five or more individual N_2O 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_2O 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_2O 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 to a gas chromatograph (GC) at five-minute intervals for the 20 minute of chamber closure. The GC included thermal conductivity, electron capture and flame ionization detectors for measuring CO_2, N_2O and CH_4 concentrations, respectively. Also during that time, flux gradient measurements by Fourier Transform Infrared spectroscopy (FTIR) showed that CO_2, N_2O and CH_4 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, Barba et al., 2019; Courtois et al., 2019, O'Connell et al 2018, 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 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_2O 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 a 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 chamber-based 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_2O pulses, which can generate the bulk of environmentally-relevant net N_2O 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_2O 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_2O 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_2O molecules (Yoshida and Toyoda 2000; Harris *et al.* 2020). Isotopic N_2O and site-preference measurements can provide important information about the environmental sources of N_2O 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_2O 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_2O 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 H_2O, 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 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_2O 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 sub-plot quadrats, seasonally, or quarterly) so as to avoid inserting bias towards 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 CRDS 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 N_2O 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 Holtta 2010). In these two examples, high frequency soil CO_2 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_2O 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_2O 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 analyser (Grace *et al.* 2020), was central to this finding: N_2O 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_2O emission (Scheer *et al.* 2017). During the growing season, fertilizer-derived N_2O 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_2O 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_2O 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_2O reduction in well-drained soils warrants an improved understanding of spatial heterogeneity of anaerobic microsites where N_2O can get reduced to N_2 via biological denitrification (Parkin 1987). Representation of spatial heterogeneity is crucial for upscaling mechanistic processes related to N_2O 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 land-surface 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 N_2O 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 N_2O 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 N_2O 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 N_2O fluxes by process-based biogeochemical models (Myrgiotis *et al.* 2018; Sihi *et al.* 2019). Alternatively, process-based models coupled with machine-learning approaches can be used to evaluate N_2O dynamics and driver-response relationships in long-term high-frequency N_2O 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 N_2O fluxes from high-frequency 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 N_2O 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_2O Database (https://ecoapps.nrel.colostate.edu/global_n2o/; (Dorich *et al.* 2020)) holds promise to lower uncertainty in annual N_2O 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 high-frequency 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 (https://ameriflux.lbl.gov) and FluxNet (https://fluxnet.org) can potentially increase the user pool of the Global N_2O Database and improve the flux processing pipelines and gap-filling algorithms. Institutional back-up, built-in 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_2O data.

Future directions

Rethinking nitrogen cycle processes and budgets

Hot spots and hot moments of soil N_2O emissions can account for large proportions of total ecosystem N_2O 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_2), Figure 1). Such designs can quantify the importance of soil N_2O hot moments and what abiotic conditions correlate with those fluxes: in a Northern California grassland system, >80% of the emitted N_2O 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 N_2O 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 N_2O flux events *in situ* provides an excellent template to explore the molecular and microbial dynamics of N_2O production and consumption in soils. With the proliferation of high-frequency soil N_2O emissions data, laboratory incubation experiments (using natural abundance stable isotopes or ^{13}C or ^{15}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 N_2O production and consumption under simulated field conditions (Yang *et al.* 2012) which would help produce better estimates of denitrification-derived N_2 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_2O 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 N_2O concentration increase in the past 4 decades (Tian *et al.* 2020). Measurements of the isotopic composition of N_2O in the global atmosphere combined with knowledge of the "isotopic fingerprints" of N_2O 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 N_2O concentrations (Pérez *et al.* 2001; Park *et al.* 2012; Snider *et al.* 2015; Prokopiou *et al.* 2018). Changes over time show increased atmospheric N_2O 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_2O isotopic composition from agricultural systems can capture the N_2O isotopic fingerprint of high flux events, which can constrain the relative contribution of fertilizer-derived N_2O 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_2O 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_2O 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_2O emissions; improved N_2O 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_2O 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 N_2O fluxes and discrete soil physicochemical measurements (R^2 values between 0.37 to 0.39, Hamrani *et al.* 2020, Glenn *et al.* 2021). Therefore, to better assess N_2O flux prediction robustness of available models (ML algorithms, statistical, process-based and Bayesian modeling approaches) high frequency data of both N_2O 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, NH_4^+ and NO_3^- become available (Figure 2).

High frequency measurements of driving variables are needed as inputs to ML models. Moisture, temperature, and O_2 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 ~$3-10k USD each depending on their features. Soil sensors (e.g., O_2, 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.

Conclusions

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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Figures/Tables

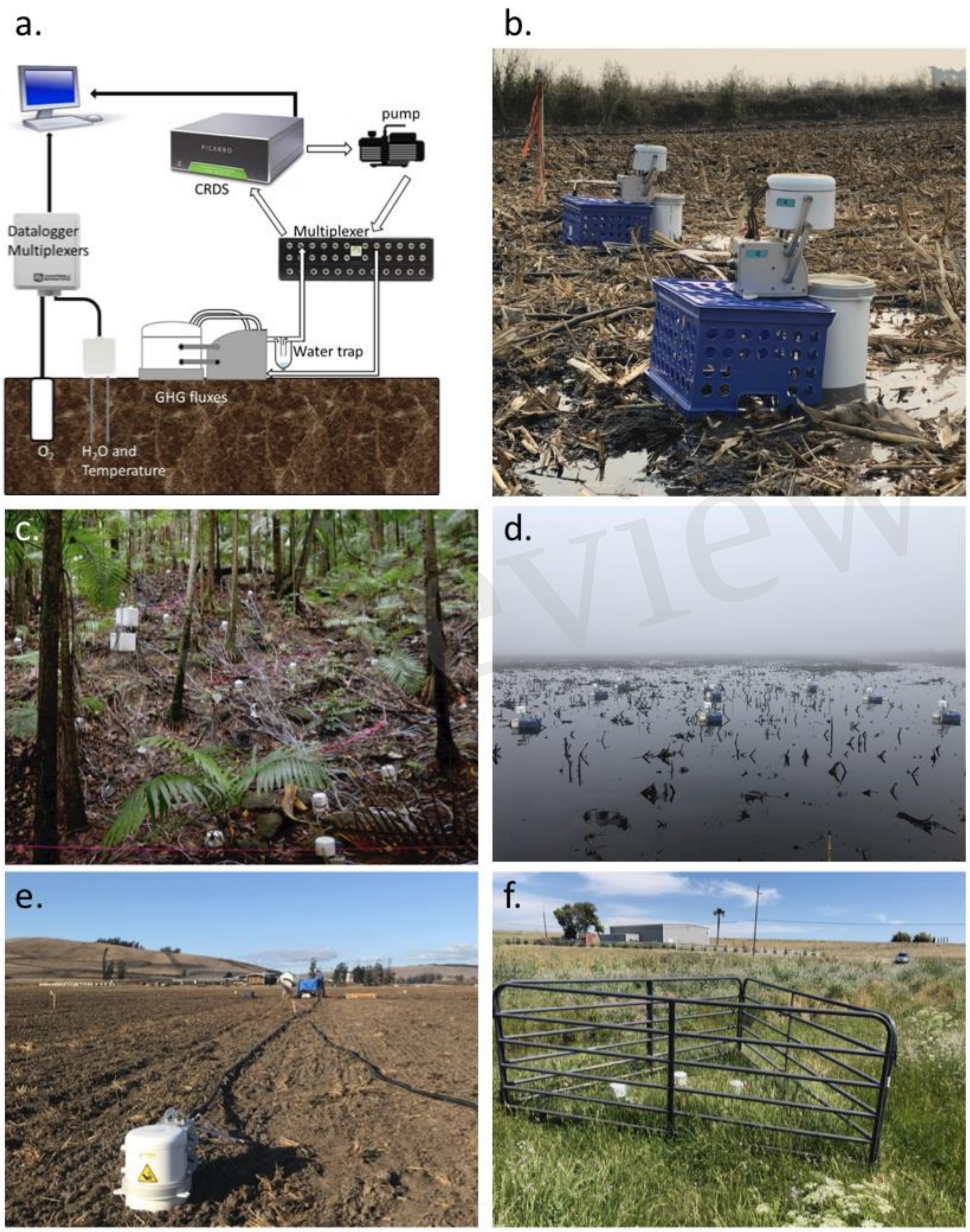

Figure 1. (a) Sampling configuration for continuous soil GHG emissions by CRDS and applicable soil physicochemical variables (in this case, e.g., soil moisture, temperature, and oxygen sensors). A circulating pump draws air after chamber enclosure. The air passes through a multiplexer where is directed 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, USA (b, d)) and agricultural systems (California, USA (e, f)).

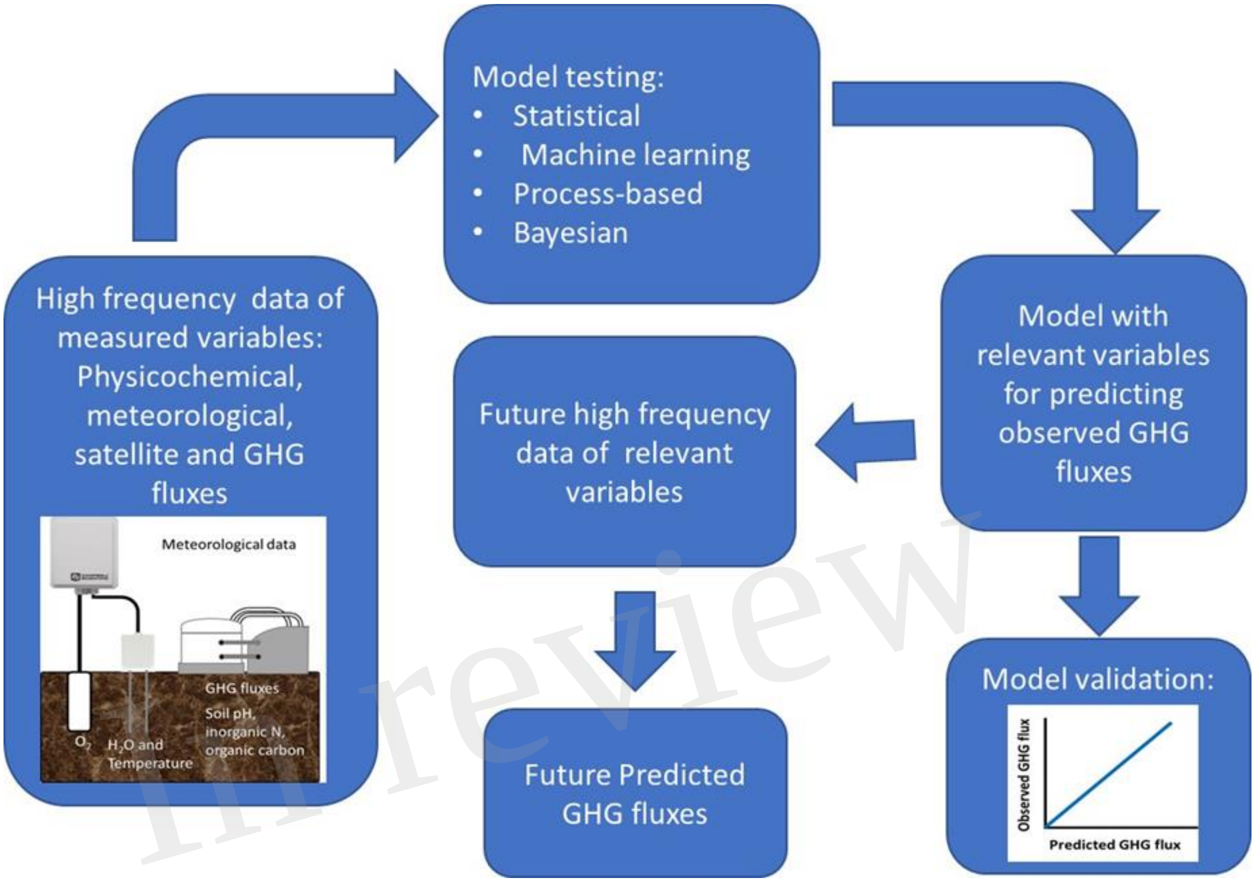

Figure 2. Diagram for testing effectiveness of available models to predict GHG fluxes. High frequency data of measured variables are required to test methods and rank them according to predictive power and computational cost.

Table 1. Pioneer methods for automated greenhouse gas fluxes measurements.

Method	Greenhouse Gas	Number of chambers	Flux measurement time (min)	Reference
Gas chromatography	CH_4, CO_2, N_2O	6	48	Silvola et al (1992)
Gas chromatography	N_2O	8	35	Crill et al (2000)
Gas chromatography	CH_4, N_2O	5	24	Butemback Ball et al (1998)
Gas chromatography	N_2O	6	30	Akiyama et al (2000)
Non-dispersive infrared spectroscopy	CO_2	10	18	Goulden and Crill (1997)
Non-dispersive infrared spectroscopy, gas chromatography	CH_4, CO_2, N_2O	6	30	Nishimura et al (2005)
Fourier Transform Infrared Spectroscopy	CH_4, CO_2, N_2O	N/A	N/A	Griffith and Galle (2000)*

(*) Flux-gradient technique

References

Anthony TL and Silver WL. 2021. Hot moments drive extreme nitrous oxide and methane emissions from agricultural peatlands. *Glob Change Biol* **27**: 5141–53.

Barba J, Poyatos R, and Vargas R. 2019. Automated measurements of greenhouse gases fluxes from tree stems and soils: magnitudes, patterns and drivers. *Sci Rep*: 1–13.

Barcellos D, O'Connell C, Silver W, *et al.* 2018. Hot Spots and Hot Moments of Soil Moisture Explain Fluctuations in Iron and Carbon Cycling in a Humid Tropical Forest Soil. *Soil Syst* **2**: 59–22.

Barton L, Wolf B, Rowlings D, *et al.* 2015. Sampling frequency affects estimates of annual nitrous oxide fluxes. *Sci Rep* **5**: 15912–9.

Bernhardt ES, Blaszczak JR, Ficken CD, *et al.* 2017. Control Points in Ecosystems: Moving Beyond the Hot Spot Hot Moment Concept. *Ecosystems* **20**: 665–82.

Bond Lamberty B, Christianson DS, Malhotra A, *et al.* 2020. COSORE: A community database for continuous soil respiration and other soil-atmosphere greenhouse gas flux data. *Glob Change Biol* **26**: 7268–83.

Brachmann CG, Hernandez-Ramirez G, and Hik DS. 2020. CH4 uptake along a successional gradient in temperate alpine soils. *Biogeochemistry* **147**: 109–23.

Brannon EQ, Moseman-Valtierra SM, Rella CW, *et al.* 2016. Evaluation of laser-based spectrometers for greenhouse gas flux measurements in coastal marshes. *Limnol Oceanogr Methods* **14**: 466–76.

Butterbach-Bahl K, Baggs EM, Dannenmann M, *et al.* 2013. Nitrous oxide emissions from soils: how well do we understand the processes and their controls? *Phil Trans R Soc B* **368**: 20130122–13.

Chapuis-Lardy L, Wrage N, Metay A, *et al.* 2007. Soils, a sink for N2O? A review. *Glob Change Biol* **13**: 1–17.

Christiansen JR, Outhwaite J, and Smukler SM. 2015. Comparison of CO2, CH4 and N2O soil-atmosphere exchange measured in static chambers with cavity ring-down spectroscopy and gas chromatography. *Agricultural and Forest Meteorology* **211-212**: 48–57.

Courtois EA, Stahl C, Burban B, *et al.* 2019. Automatic high-frequency measurements of full soil greenhouse gas fluxes in a tropical forest. *Biogeosciences* **16**: 785–96.

Cowan N, Levy P, Maire J, *et al.* 2020. An evaluation of four years of nitrous oxide fluxes after application of ammonium nitrate and urea fertilisers measured using the eddy covariance method. *Agricultural and Forest Meteorology* **280**: 107812.

Creelman C, Nickerson N, and Risk D. 2013. Quantifying Lateral Diffusion Error in Soil Carbon Dioxide Respiration Estimates using Numerical Modeling. *Soil Science Society of America Journal* **77**: 699–.

Curiel Yuste J, Baldocchi DD, Gershenson A, *et al.* 2007. Microbial soil respiration and its dependency on carbon inputs, soil temperature and moisture. *Glob Change Biol* **13**: 2018–35.

Decock C and Six J. 2013. On the potential of δ 18O and δ 15N to assess N 2O reduction to N 2in soil. *Eur J Soil Sci* **64**: 610–20.

Diefenderfer HL, Cullinan VI, Borde AB, *et al.* 2018. High-frequency greenhouse gas flux measurement system detects winter storm surge effects on salt marsh. *Glob Change Biol* **24**: 5961–71.

Dorich CD, Conant RT, Albanito F, *et al.* 2020. Improving N2O emission estimates with the global N2O database. *Current Opinion in Environmental Sustainability* **47**: 13–20.

Eberwein JR, Homyak PM, Carey CJ, *et al.* 2020. Large nitrogen oxide emission pulses from desert soils and associated microbiomes. *Biogeochemistry* **149**: 239–50.

Ebrahimi A and Or D. 2018. On Upscaling of Soil Microbial Processes and Biogeochemical Fluxes From Aggregates to Landscapes. *J Geophys Res Biogeosci* **123**: 1526–47.

Erler DV, Duncan TM, Murray R, *et al.* 2015. Applying cavity ring-down spectroscopy for the measurement of dissolved nitrous oxide concentrations and bulk nitrogen isotopic composition in aquatic systems: Correcting for interferences and field application. *Limnol Oceanogr Methods* **13**: 391–401.

Eugster W, Zeyer K, Zeeman M, *et al.* 2007. Methodical study of nitrous oxide eddy covariance measurements using quantum cascade laser spectrometery over a Swiss forest. *Biogeosciences* **4**: 927–39.

Gaillard RK, Jones CD, Ingraham P, *et al.* 2018. Underestimation of N2O emissions in a comparison of the DayCent, DNDC, and EPIC models. *Ecol Appl* **28**: 694–708.

Gerber JS, Carlson KM, Makowski D, *et al.* 2016. Spatially explicit estimates of N 2O emissions from croplands suggest climate mitigation opportunities from improved fertilizer management. *Glob Change Biol* **22**: 3383–94.

Glenn AJ, Moulin AP, Roy AK, and Wilson HF. 2021. Soil nitrous oxide emissions from no-till canola production under variable rate nitrogen fertilizer management. *Geoderma* **385**: 114857.

Goldberg SD and Gebauer G. 2009. Drought turns a Central European Norway spruce forest soil from an N2O source to a transient N2O sink. *Glob Change Biol* **15**: 850–60.

Görres CM, Kammann C, and Ceulemans R. 2016. Automation of soil flux chamber measurements: potentials and pitfalls. *Biogeosciences* **13**: 1949–66.

Grace PR, Weerden TJ, Rowlings DW, *et al.* 2020. Global Research Alliance N2O chamber methodology guidelines: Considerations for automated flux measurement. *J environ qual* **49**: 1126–40.

Griffis TJ, Chen Z, Baker JM, *et al.* 2017. Nitrous oxide emissions are enhanced in a warmer and wetter world. *PNAS* **114**: 12081–5.

Griffith DWT and Galle B. 2000. Flux measurements of NH3, N2O and CO2 using dual beam FTIR spectroscopy and the flux-gradient technique. *Atmospheric Environment* **34**: 1087–98.

Groffman PM, Butterbach-Bahl K, Fulweiler RW, *et al.* 2009. Challenges to incorporating spatially and temporally explicit phenomena (hotspots and hot moments) in denitrification models. *Biogeochemistry* **93**: 49–77.

Hamrani A, Akbarzadeh A, and Madramootoo CA. 2020. Machine learning for predicting greenhouse gas emissions from agricultural soils. *Sci Total Environ* **741**: 140338–.

Harris SJ, Liisberg J, Xia L, *et al.* 2020. N2O isotopocule measurements using laser spectroscopy: analyzer characterization and intercomparison. *Atmospheric Measurement Techniques* **13**: 2797–831.

Heil J, Wolf B, Brüggemann N, *et al.* 2014. Site-specific 15N isotopic signatures of abiotically produced N2O. *Geochimica et Cosmochimica Acta* **139**: 72–82.

Hemes KS, Chamberlain SD, Eichelmann E, *et al.* 2019. Assessing the carbon and climate benefit of restoring degraded agricultural peat soils to managed wetlands. *Agricultural and Forest Meteorology* **268**: 202–14.

Jeffrey LC, Reithmaier G, Sippo JZ, *et al.* 2019. Are methane emissions from mangrove stems a cryptic carbon loss pathway? Insights from a catastrophic forest mortality. *New Phytol* **224**: 146–54.

Keane BJ, Ineson P, Vallack HW, *et al.* 2018. Greenhouse gas emissions from the energy crop oilseed rape (Brassica napus); the role of photosynthetically active radiation in diurnal N2O flux variation. *GCB Bioenergy*.

Kim DG, Vargas R, Bond-Lamberty B, and Turetsky MR. 2012. Effects of soil rewetting and thawing on soil gas fluxes: a review of current literature and suggestions for future research. *Biogeosciences* **9**: 2459–83.

Krichels AH and Yang WH. 2019. Dynamic Controls on Field-Scale Soil Nitrous Oxide Hot Spots and Hot Moments Across a Microtopographic Gradient. *J Geophys Res Biogeosci* **124**: 3618–34.

Kuzyakov Y and Blagodatskaya E. 2015. Microbial hotspots and hot moments in soil: Concept & review. *Soil Biology and Biochemistry* **83**: S29–S36.

Lebegue B, Schmidt M, Ramonet M, *et al.* 2016. Comparison of nitrous oxide (N2O) analyzers for high-precision measurements of atmospheric mole fractions. *Atmospheric Measurement Techniques* **9**: 1221–38.

Liang LL, Grantz DA, and Jenerette GD. 2016. Multivariate regulation of soil CO 2and N 2O pulse emissions from agricultural soils. *Glob Change Biol* **22**: 1286–98.

Liptzin D, Silver WL, and Detto M. 2010. Temporal Dynamics in Soil Oxygen and Greenhouse Gases in Two Humid Tropical Forests. *Ecosystems* **14**: 171–82.

Liu H, Zak D, Rezanezhad F, and Lennartz B. 2019. Soil degradation determines release of nitrous oxide and dissolved organic carbon from peatlands. *Environ Res Lett* **14**: 094009–10.

Livesley SJ, Grover S, Hutley LB, *et al.* 2011. Seasonal variation and fire effects on CH4, N2O and CO2 exchange in savanna soils of northern Australia. *Agricultural and Forest Meteorology* **151**: 1440–52.

Martin JG, Phillips CL, Schmidt A, *et al.* 2012. High-frequency analysis of the complex linkage between soil CO(2) fluxes, photosynthesis and environmental variables. *Tree Physiol* **32**: 49–64.

Matson AL, Corre MD, Langs K, and Veldkamp E. 2017. Soil trace gas fluxes along orthogonal precipitation and soil fertility gradients in tropical lowland forests of Panama. *Biogeosciences* **14**: 3509–24.

Mencuccini M and Hölttä T. 2010. The significance of phloem transport for the speed with which canopy photosynthesis and belowground respiration are linked. *New Phytol* **185**: 189–203.

Molodovskaya M, Singurindy O, Richards BK, *et al.* 2012. Temporal Variability of Nitrous Oxide from Fertilized Croplands: Hot Moment Analysis. *Soil Science Society of America Journal* **76**: 1728–40.

Mosier A, Kroeze C, Nevison C, *et al.* 1998. Closing the global N2O budget: nitrous oxide emissions through the agricultural nitrogen cycle. *Nutrient Cycling in Agroecosystems*.

Murray R, Erler D, Rosentreter J, *et al.* 2018. A seasonal source and sink of nitrous oxide in mangroves: Insights from concentration, isotope, and isotopomer measurements. *Geochimica et Cosmochimica Acta* **238**: 169–92.

Myrgiotis V, Williams M, Topp CFE, and Rees RM. 2018. Improving model prediction of soil N2O emissions through Bayesian calibration. *Sci Total Environ* **624**: 1467–77.

O’Connell CS, Ruan L, and Silver WL. 2018. Drought drives rapid shifts in tropical rainforest soil biogeochemistry and greenhouse gas emissions. *Nature Communications*: 1–9.

Park S, Croteau P, Boering KA, *et al.* 2012. Trends and seasonal cycles in the isotopic composition of nitrous oxide since 1940. *Nature Geosci* **5**: 261–5.

Parkin TB. 1987. Soil Microsites as a Source of Denitrification Variability. *Soil Science Society of America Journal* **51**: 1194–9.

Parkin TB. 2008. Effect of Sampling Frequency on Estimates of Cumulative Nitrous Oxide Emissions. *J environ qual* **37**: 1390–5.

Pattey E, Edwards GC, Desjardins RL, *et al.* 2007. Tools for quantifying N2O emissions from agroecosystems. *Agricultural and Forest Meteorology* **142**: 103–19.

Pérez T, Trumbore SE, Tyler SC, *et al.* 2001. Identifying the agricultural imprint on the global N2O budget using stable isotopes. *J Geophys Res Atmos* **106**: 9869–78.

Prokopiou M, Sapart CJ, Rosen J, *et al.* 2018. Changes in the Isotopic Signature of Atmospheric Nitrous Oxide and Its Global Average Source During the Last Three Millennia. *J Geophys Res Atmos* **123**: 131–17.

Rapson TD and Dacres H. 2014. Analytical techniques for measuring nitrous oxide. *Trends in Analytical Chemistry* **54**: 65–74.

Reeves S and Wang W. 2015. Optimum sampling time and frequency for measuring N2O emissions from a rain-fed cereal cropping system. *Sci Total Environ* **530-531**: 219–26.

Reeves S, Wang W, Salter B, and Halpin N. 2016. Quantifying nitrous oxide emissions from sugarcane cropping systems: Optimum sampling time and frequency. *Atmospheric Environment* **136**: 123–33.

Ruan L and Robertson GP. 2016. Reduced Snow Cover Increases Wintertime Nitrous Oxide (N2O) Emissions from an Agricultural Soil in the Upper U.S. Midwest. *Ecosystems* **20**: 917–27.

Saha D, Basso B, and Robertson GP. 2021. Machine learning improves predictions of agricultural nitrous oxide (N 2O) emissions from intensively managed cropping systems. *Environ Res Lett* **16**: 024004.

Saha D, Kemanian AR, Montes F, *et al.* 2018. Lorenz Curve and Gini Coefficient Reveal Hot Spots and Hot Moments for Nitrous Oxide Emissions. *J Geophys Res Biogeosci* **123**: 193–206.

Saha D, Kemanian AR, Rau BM, *et al.* 2017. Designing efficient nitrous oxide sampling strategies in agroecosystems using simulation models. *Atmospheric Environment* **155**: 189–98.

Savage KE and Davidson EA. 2003. A comparison of manual and automated systems for soil CO2 flux measurements: trade-offs between spatial and temporal resolution. *J Exp Bot* **54**: 891–9.

Savage K, Phillips R, and Davidson E. 2014. High temporal frequency measurements of greenhouse gas emissions from soils. *Biogeosciences* **11**: 2709–20.

Scheer C, Rowlings D, Firrell M, *et al.* 2017. Nitrification inhibitors can increase post-harvest nitrous oxide emissions in an intensive vegetable production system. : 1–9.

Schlesinger WH. 2013. An estimate of the global sink for nitrous oxide in soils. *Glob Change Biol* **19**: 2929–31.

Shcherbak I, Millar N, and Robertson GP. 2014. Global metaanalysis of the nonlinear response of soil nitrous oxide (N2O) emissions to fertilizer nitrogen. *Proceedings of the National Academy of Sciences* **111**: 9199–204.

Sihi D, Davidson EA, Savage KE, and Liang D. 2019. Simultaneous numerical representation of soil microsite production and consumption of carbon dioxide, methane, and nitrous oxide using probability distribution functions. *Glob Change Biol* **26**: 200–18.

Silver WL, Lugo AE, and Keller M. 1999. Soil oxygen availability and biogeochemistry along rainfall and topographic gradients in upland wet tropical forest soils. *Biogeochemistry* **44**: 301–28.

Silvola J, Martikainen P, and Nykänen H. 1992. A mobile automatic gas chromatograph system to measure CO2, CH4 and N2O fluxes from soil in the field. *Suo* **43**: 263–6.

Smith KA and Dobbie KE. 2001. The impact of sampling frequency and sampling times on chamber-based measurements of N2O emissions from fertilized soils. *Glob Change Biol* **7**: 933–45.

Snider DM, Venkiteswaran JJ, Schiff SL, and Spoelstra J. 2015. From the ground up: global nitrous oxide sources are constrained by stable isotope values. (S Hu, Ed). *PLoS One* **10**: e0118954–.

Sui Y, Atreya M, Dahal S, *et al.* 2021. Controlled Biodegradation of an Additively Fabricated Capacitive Soil Moisture Sensor. *ACS Sust Chem Eng*.

Syakila A and Kroeze C. 2011. The global nitrous oxide budget revisited. *Greenhouse Gas Measurement and Management* **1**: 17–26.

Tallec T, Brut A, Joly L, *et al.* 2019. N2O flux measurements over an irrigated maize crop: A comparison of three methods. *Agricultural and Forest Meteorology* **264**: 56–72.

Teh YA, Silver WL, Sonnentag O, *et al.* 2011. Large Greenhouse Gas Emissions from a Temperate Peatland Pasture. *Ecosystems* **14**: 311–25.

Tian H, Xu R, Canadell JG, *et al.* 2020. A comprehensive quantification of global nitrous oxide sources and sinks. *Nature*: 1–24.

Tian H, Yang J, Lu C, *et al.* 2018. The Global N2O Model Intercomparison Project. *Bulletin of the American Meteorological Society* **99**: 1231–51.

Turner PA, Griffis TJ, Mulla DJ, *et al.* 2016. A geostatistical approach to identify and mitigate agricultural nitrous oxide emission hotspots. *Science of the Total Environment* **572**: 442–9.

Vargas R, Sánchez-Cañete P E, Serrano-Ortiz P, *et al.* 2018. Hot-Moments of Soil CO2 Efflux in a Water-Limited Grassland. *Soil Syst* **2**: 47–18.

Wagner-Riddle C, Baggs EM, (null) TC, *et al.* 2020. Mitigation of nitrous oxide emissions in the context of nitrogen loss reduction from agroecosystems: managing hot spots and hot moments. *Current Opinion in Environmental Sustainability*.

Wagner-Riddle C, Congreves KA, Abalos D, *et al.* 2017. Globally important nitrous oxide emissions from croplands induced by freeze–thaw cycles. *Nature Geosci* **10**: 279–83.

Winther M, Balslev-Harder D, Christensen S, *et al.* 2018. Continuous measurements of nitrous oxide isotopomers during incubation experiments. *Biogeosciences* **15**: 767–80.

Yang WH, Weber KA, and Silver WL. 2012. Nitrogen loss from soil through anaerobic ammonium oxidation coupled to iron reduction. *Nature Geosci* **5**: 538–41.

Yoshida N and Toyoda S. 2000. Constraining the atmospheric N2O budget from intramolecular site preference in N2O isotopomers. *Nature* **405**: 330–4.

Figure 1.TIFF

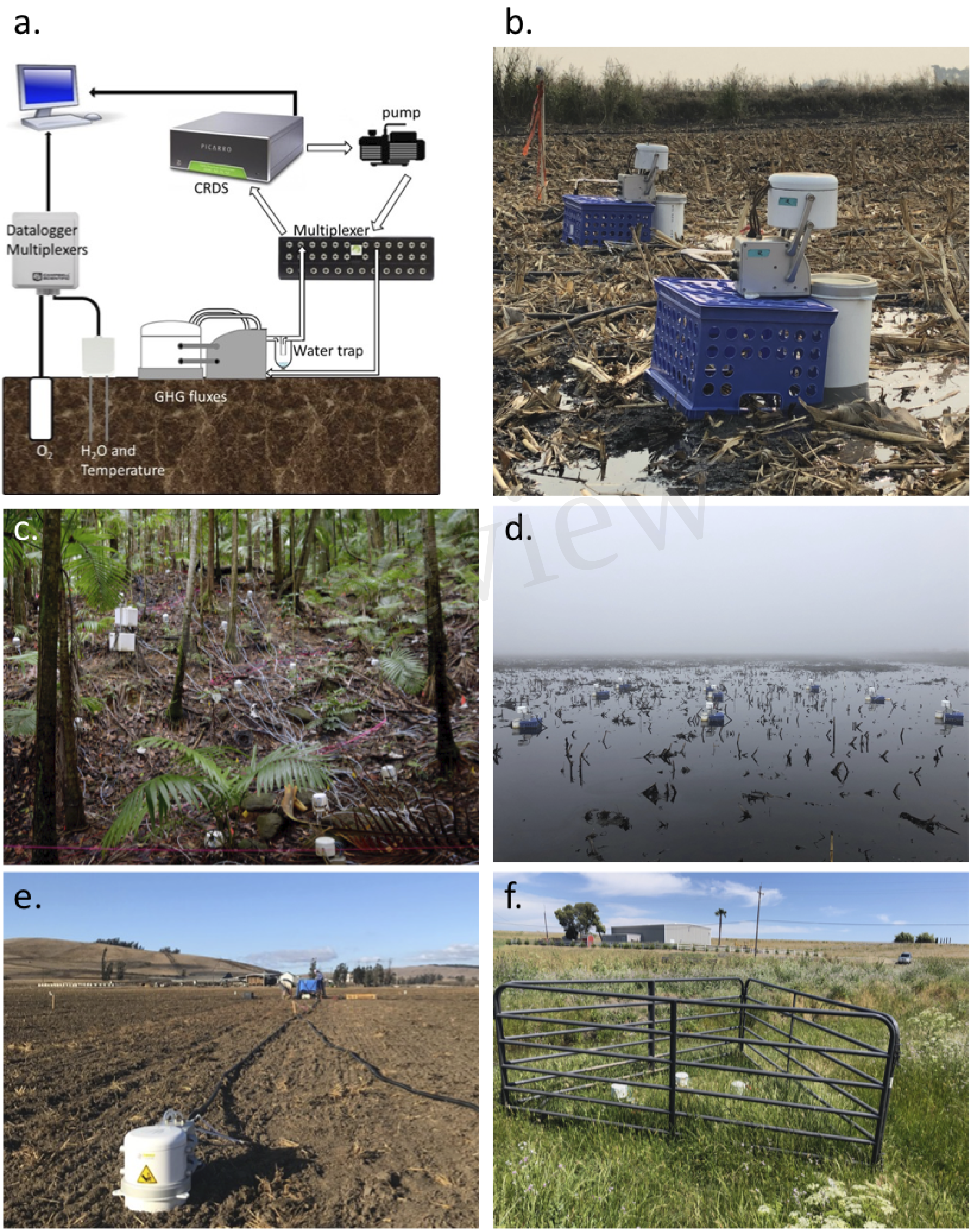

Figure 2.TIFF