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Sampling Frequency for Decreasing Uncertainty in Estimating Annual Nitrous Oxide

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Quantifying nitrous oxide (N_2O) fluxes, a potent greenhouse gas, from soils is necessary to improve our knowledge of terrestrial N_2O losses. Quantifying annual N_2O fluxes is challenging as daily fluxes are renowned for their high temporal and spatial variability due multiple factors regulating N_2O production and consumption in soils [2]. Manual (static) chambers are the most widely used technique for quantifying daily N_2O emissions as the N_2O fluxes are orders of magnitudes smaller than carbon dioxide fluxes and the accumulation of gas in the chamber headspace leads to the best results with respect to flux detection limits [3]. Frequency of sampling is critical when determining annual N_2O fluxes and associated emission factors using manual chambers. The introduction of automated chambers has enabled researchers to better characterise temporal variation in N_2O fluxes, and utilising these datasets provides a unique opportunity to investigate the effect of sample frequency on estimates of annual N_2O fluxes. The aim of the following research was to investigate the effect of sampling frequency on estimates of annual soil N_2O fluxes using 28 published datasets of subdaily N_2O fluxes from a variety of different terrestrial ecosystems across the globe.

Study sites varied geographically (Australia, China and Germany), and included 28 data sets from agricultural and forest soils in temperate, semiarid and subtropical climates (Table 1) [1]. Annual fluxes based on subdaily N_2O fluxes ranged from <0.1 to 8.1 kg N ha^{-1} yr^{-1} depending on the study site, and were calculated using at least three replicate chambers per experimental treatment. The effect of sampling frequency on estimates of annual N_2O-N fluxes was assessed using a modified jackknife technique [4,5]. Average daily flux measurements were calculated for each replicate chamber in each dataset from the sub-daily flux measurements as we did not consistently observe diurnal flux variations at each location. Each site's daily flux population was subsequently subsampled daily ('best estimate'), three times per week, weekly, bi-weekly and 4-weekly, and for each permutation of the time interval, for each dataset. Estimates of annual N_2O-N flux for a given chamber, site and frequency permutation were then calculated by linear interpolation and integration of daily fluxes with time. Missing

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Table 1. Key characteristics of data sets used to assess the effect of sampling frequency on annual N_2O fluxes and the minimum sampling frequencies needed to achieve 10% accuracy (adapted from [1])

Location	Datasets (No.Years, No.Treatments)	Climate	Landuse	Annual N_2O flux (kg N ha^{-1})	Episodicity[a]	Minimum sampling frequency to achieve 10% accuracy		
						Jackknife analysis: Frequency	Jackknife analysis: No. days	Informed sampling: No. days
Bellenden Kerr, Australia	One (1, 1)	Tropical	Forest	1.16	Moderate	Weekly	52	156
Mooloolah Valley, Australia	Five (3, 2)	Sub-tropical	Forest, Pasture, Orchard	0.48–8.12	Moderate–High	Daily–3 days a week	156–365	Not determined
Höglwald, Germany	Two (1, 1)	Temperate	Plantation forest	0.58–2.46	High	Daily–3 days a week	156	83
Xilin, Inner Mongolia	One (1)	Semi-arid	Steppe grassland	0.21	Extreme	3 days a week	156	Not determined
Cunderdin, Australia	Eight (4, 2)	Semi-arid	Cereal cropping	0.08–0.16	High–Extreme	Daily–3 days a week	156–365	Not determined
Kingsthorpe, Australia	Three (1, 3)	Sub-tropical	Irrigated cereal-cotton cropping	2.61–2.93	High–Extreme	Daily–3 days a week	365	Not determined
Wongan Hills, Australia	Eight (2, 4)	Semi-arid	Cereal cropping	0.03–0.07	Extreme	Daily	365	60

[a] Episodicity determined using coefficient of the mean daily flux: Moderate, CV > 50–100%); high, CV >100–200%; extreme, CV >200%.

data was not replaced. The average annual flux estimate (calculated from replicated chambers) from each sampling frequency and permutation, and for each dataset, was then compared against the 'best estimate' annual flux (expressed as a %) so as the access the accuracy of the sampling frequencies. In addition, we estimated annual N_2O fluxes for three of our datasets based on the authors informed understanding of the factor driving daily losses.

Annual N_2O fluxes calculated from the average daily fluxes, which is used here as the reference annual flux, varied from 0.03 kg N_2O-N ha^{-1} yr^{-1} to 8.1 kg N_2O-N ha^{-1} yr^{-1} (Table 1). Daily N_2O fluxes were highly variable within each dataset, but more so for some; the coefficient of variation (CV) of the mean daily N_2O flux ranged from 78% for a subtropical rainforest to 913% for a semiarid soil planted to a grain legume (Table 1). The variation in daily means was not related to the magnitude of the annual N_2O flux, but instead reflected the episodic nature of the daily fluxes for a particular study site. We subsequently classified the data sets as having either moderate (CV>50–100%), high (CV>100–200%) or extreme (CV>200%) 'episodicity' based on the CV of the mean daily flux (Table 1).

The minimum sampling frequency required to robustly estimate an annual N_2O flux varied depending upon the 'episodicity' of the dataset and the required accuracy (Table 1). Twenty, or 74%, of the datasets required daily sampling to achieve an annual N_2O flux value within 10% of the best estimate. In only one case (tropical rainforest, Bellenden Ker), and when the daily N_2O flux CV was relatively low (78%), did weekly sampling result in annual N_2O flux within 10% of the best estimate. Generally speaking, highly or extremely episodic data sets (CV>100%) required sampling either daily or 3 days a week. Lowering the desired accuracy decreased the required frequency of sampling, however 89% of the data sets still needed to be sampled at least weekly to achieve ±30% accuracy. Annual N_2O fluxes estimated by the authors' based on their understanding of the factors driving daily losses did not vary statistically from the 'best' estimate calculated using all daily fluxes. However, the informed sampling approach still required sampling to occur every 2 to 6 days depending on the dataset (Table 1).

In conclusion, daily sampling is largely required to achieve annual N_2O fluxes within 10% of the 'best' estimate. Decreasing the regularity of measurements either under- or overestimated annual N_2O fluxes, with a maximum overestimation of 935%. The frequency of sampling required to accurately calculate an annual N_2O flux will depend on the episodic nature of the N_2O flux at the study site of interest, rather than the magnitude of the annual flux. Measurement frequency could be lowered using an informed sampling strategy based on environmental factors known to affect temporal variability, but still required sampling more than once a week.

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