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Hot or Not? An Evaluation of Methods for Identifying Hot Moments of Nitrous Oxide Emissions From Soils

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Key Points:

- When comparing approaches (1.5x IQR, IF, 2 SD, and 4 SD) to identify N_2O hot moment thresholds, 1.5x IQR best identified the hot moments
- Subdividing the N_2O flux data sets by season (early, late, and non-growing season) was not necessary to improve hot moment identification
- To standardize identification of N_2O hot moments from high spatiotemporal resolution data sets, use 1.5x IQR on whole year N_2O fluxes

Supporting Information:

Supporting Information may be found in the online version of this article.

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Abstract Effectively quantifying hot moments of nitrous oxide (N_2O) emissions from agricultural soils is critical for managing this potent greenhouse gas. However, we are challenged by a lack of standard approaches for identifying hot moments, including (a) determining thresholds above which emissions are considered hot moments, and (b) considering seasonal variation in the magnitude and frequency distribution of net N_2O fluxes. We used one year of hourly N_2O flux measurements from 16 autochambers that varied in flux magnitude and frequency distribution in a conventionally tilled maize field in central Illinois, USA, to compare three approaches to identify hot moment thresholds: standard deviations (SD) above the mean, 1.5x the interquartile range (IQR), and isolation forest (IF) identification of anomalous values. We also compared these approaches on seasonally subdivided data (early, late, and non-growing seasons) versus the whole year. Our analyses revealed that 1.5x IQR method best identified N_2O hot moments. In contrast, using 2 or 4 SD both yielded hot moment threshold values too high, and IF yielded threshold values too low, leading to missed N_2O hot moments or low net N_2O fluxes mischaracterized as hot moments, respectively. Furthermore, seasonally subdividing the data set not only facilitated identification of smaller hot moments in the late- and non-growing seasons when N_2O hot moments were generally smaller but it also increased hot moment threshold values in the early growing season when N_2O hot moments were larger. Consequently, of the methods evaluated here, we recommend using the 1.5x IQR method on whole year data sets to identify N_2O hot moments.

Plain Language Summary Nitrous oxide (N_2O) is a greenhouse gas that traps 273 times more heat in Earth's atmosphere than carbon dioxide (CO_2). Microbes in the soil produce N_2O, sometimes with short bursts of high production, called "hot moments." Hot moments are stimulated by environmental triggers such as rainfall or fertilization. Management strategies targeting hot moments can be particularly effective in reducing cumulative annual soil N_2O emissions from agricultural fields. However, to date there is no standard approach to identifying hot moments. Here, we analyzed 16 one-year data sets of hourly N_2O emission measurements from a large area in one maize field to compare different methods that are used to identify hot moments of N_2O. We learned that the threshold values above which N_2O emissions would be considered hot moments were best determined as 1.5 times greater than the N_2O emission value that fell in the middle of the spread of emission values in the data set, a method called "1.5x the interquartile range." We could also best identify hot moments of N_2O when we analyzed the whole year N_2O data sets as opposed to seasonally subdividing the data sets. Our recommendations to standardize N_2O hot moment identification will facilitate synthesis of knowledge across studies.

1. Introduction

Nitrous oxide (N_2O) currently accounts for 6% of Earth's radiative forcing (Dutton et al., 2023), and soil emissions contribute significantly to rising atmospheric concentrations of this potent greenhouse gas. Soil N_2O emissions are often characterized by short periods of high reaction rates that contribute disproportionately to cumulative annual N_2O emissions, referred to as hot moments (Bernhart et al., 2015; Groffman et al., 2009; Wagner-Riddle et al., 2020). Hot moments are prime targets for land management practices to mitigate N_2O emissions, especially in agroecosystems (Wagner-Riddle et al., 2020). However, there is high uncertainty in the effectiveness of agricultural land management practices in reducing emissions, in part because assessments largely rely on

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relatively infrequent manual chamber-based emissions measurements that may miss many of the hot moments (Charteris et al., 2020; Kravchenko & Robertson, 2015). Understanding N_2O hot moments from high temporal resolution data sets derived from autochamber and micrometeorological measurements can help guide improved manual chamber measurement sampling to better capture hot moments (Anthony & Silver, 2021; Lawrence et al., 2021; Tallec et al., 2019), and help parameterize models to more accurately predict N_2O budgets on regional to global scales (O'Connell et al., 2022). Despite these data sets becoming more common (Charteris et al., 2020, Dorich et al., 2020), there currently is no standard approach for hot moment identification, and the implications of different approaches on hot moment identification and quantification have not previously been evaluated.

The concept of biogeochemical hot moments was popularized by McClain et al. (2003) over two decades ago and has inspired many studies investigating the importance and cause of N_2O hot moments (Bernhardt et al., 2017). Yet there is no consensus on N_2O hot moment identification because hot moments lack a quantitative definition. Based on the conceptual definition that hot moments are "short periods that exhibit disproportionately high reaction rates relative to longer intervening time periods" (McClain et al., 2003), most conservatively, N_2O hot moments should represent less than 50% of data points in a time series of N_2O emission measurements and emissions greater than the average of the time series. Thus, a common interpretation of N_2O hot moments is that they occur relatively rarely, only when triggered by events, such as rainfall, fertilization, or freeze-thaw (Groffman et al., 2009; Molodovskaya et al., 2012; Wagner-Riddle et al., 2017, 2020), and these events create conditions more favorable for N_2O production than baseline conditions. As such, N_2O hot moments should account for far less than 50% of the data points in N_2O emission time series, though how much less depends on the frequency of hot moment triggers in a given system. Similarly, a common interpretation of "disproportionately high reaction rates" suggests that N_2O hot moments represent emissions far greater than the average emission, though how much greater depends on the outlier detection methods used to identify N_2O hot moments as well as the magnitude and frequency distribution of the emission data sets. Given these qualitative criteria for defining N_2O hot moments in terms of the proportion of a time series attributed to hot moments and the magnitude of the emissions, it is still possible to evaluate how well quantitative hot moment identification approaches meet these dual criteria.

There are many outlier detection methods that could be used for identifying N_2O hot moments (Smiti, 2020), wherein emission values above a threshold are considered part of an N_2O hot moment. Since N_2O hot moments can be obvious in time series of net N_2O flux data, thresholds are sometimes arbitrarily determined when visualizing the data set (Mander et al., 2021; Rautakoski et al., 2024). As a more rigorous approach, statistical methods can be used to identify data points as outliers based on their deviation from a standard distribution, with standard deviation (SD) and interquartile range (IQR) methods most commonly used for N_2O hot moment identification (e.g., Anthony et al., 2023; Anthony & Silver, 2021; Anthony & Silver, 2024; Li et al., 2015; Molodovskaya et al., 2012; Palta et al., 2014; Zhou et al., 2022). The SD method identifies outliers as values exceeding a number of SDs above the mean, whereas the IQR method is typically applied by identifying outliers 1.5 times the IQR above the third quartile or below the first quartile. These two methods are distribution-based approaches that assume a normal distribution to the data set. However, this assumption belies the very behavior of N_2O hot moments (episodic and large emission pulses), which typically leads to right-skewed N_2O flux data sets. Logarithmic transformation of data sets may not be sufficient to achieve normal distributions for highly skewed data sets and cannot be applied to data sets with negative (e.g., N_2O consumption) values. The SD method is sensitive to the frequency distribution of the data set because both the standard deviation and mean are inflated in right-skewed distributions. In contrast, the IQR method is more robust against non-normal distributions. Alternatively, distribution-free methods, such as isolation forest (IF) classification, could be more appropriate for standardized hot moment identification across data sets that vary in flux magnitude and frequency distribution (Ackett et al., 2022). Isolation forest (IF) classification is a distance-based, machine learning method that uses binary trees to identify anomalous data points based on short path-lengths in the trees that indicate that the data points are few and different from the rest of the data set. These outlier detection methods have not been compared across N_2O flux data sets that vary in flux magnitude and distribution, leaving uncertain how much the methods can differ in hot moment identification and the estimated fraction of annual N_2O emissions attributed to hot moments.

In addition to considering the sensitivity of the outlier detection method to the frequency distribution of flux data, the stringency with which each of these methods is applied determines the percentage of flux measurements identified as hot moments. The stringency of the IF method can be tuned by adjusting a contamination factor, but it does not inherently lead to the identification of a certain percentage of data points as outliers in the same way as the statistical methods. For example, assuming a data set is normally distributed, using 1.5x the interquartile range (1.5x IQR; e.g., Molodovskaya et al., 2012) of the measured net N_2O fluxes, flux values higher than 99.3% of the distribution are considered part of N_2O hot moments. Using four standard deviations (4 SD) above the mean (e.g., Anthony & Silver, 2021), only flux values in the top 0.1% of the distribution are identified as hot moments. While the IQR method is typically only applied at the 1.5x IQR stringency, there is no standard stringency with which the SD method is applied. The performance of the SD method at varying stringencies therefore warrants comparison to separate this from how the SD method compares against other outlier detection methods.

Seasonal variation in N_2O flux magnitude and distribution could lead to bias in hot moment identification and quantification when considering whole year data sets compared to seasonally subdivided data sets. In agroecosystems, N_2O hot moments are largely governed by seasonally distinct triggers (Butterbach-Bahl et al., 2013). In the early growing season fertilization with ammonium (NH_4^+) or nitrate (NO_3^-) drives hot moments (Molodovskaya et al., 2012; Roy et al., 2014). Throughout the growing season, irrigation or rainfall drives hot moments (Griffis et al., 2017; Song et al., 2022). During the winter and spring, freeze-thaw and thaw drive hot moments, respectively (Risk et al., 2013; Wagner-Riddle et al., 2017). The flux magnitudes of these hot moments vary, with fertilization-driven hot moments typically yielding larger-magnitude N_2O fluxes than rainfall-driven hot moments (Kostyanovsky et al., 2019). Thaw-related hot moments can be even larger than fertilization or rainfall-driven hot moments but vary in magnitude depending on the strength of a freeze event prior to thaw (Butterbach-Bahl et al., 2002; Groffman et al., 2009). Mitigating both larger and smaller N_2O hot moments can potentially be important to reducing annual N_2O emissions, with mitigation strategies targeting the different mechanisms responsible for N_2O hot moments in different seasons. However, studies to date have conducted hot moment identification on whole year data sets such that the larger fertilization and thaw-driven N_2O emission pulses elevate the thresholds used to identify N_2O hot moments, causing the smaller, more frequent hot moments from other seasons to be missed. Because seasonally subdivided hot moment identification has not been previously conducted, it is not known how much these smaller N_2O hot moments contribute to annual N_2O emissions.

Here, we evaluated different outlier detection methods on whole year and seasonally subdivided net N_2O flux data sets to determine which approach best captured N_2O hot moments across data sets varying in N_2O flux magnitude and distribution. We chose to evaluate both commonly cited methods in the hot moment literature and a distribution-free method, as these are representative of approaches with varying inherent sensitivity to N_2O flux magnitude and distribution. We took advantage of a unique study in which one year of hourly measurements of net N_2O flux were collected from 16 autochambers located in a ∼5 ha area of a conventionally tilled maize field in central Illinois, USA. The autochambers were placed to capture variation in N_2O dynamics, including consistent N_2O cold spots and episodic N_2O hot spots (Zhang et al., 2024). The variation in N_2O flux magnitude and distribution among the 16 autochamber data sets provided the opportunity to robustly assess how hot moment identification using (a) the 2 SD or 4 SD, 1.5x IQR, and IF methods, and (b) whole year data sets versus seasonally subdivided data sets (early growing season, late growing season, and non-growing season) affected hot moment threshold values and quantification of N_2O hot moment fluxes. Based on our findings, we provide recommendations to standardize hot moment identification approaches.

2. Methods

2.1. Net N_2O Flux Data Collection

Net N_2O fluxes were measured in a commercial field located near Villa Grove, IL that was cultivated in maize-maize-soy rotations with conventional tillage and planted with maize (*Z. mays*) during the 2022 growing season. Deep chisel tillage was performed in November 2021. Pre-planting fertilizers were applied at the rate of 19.7 kg N ha^{-1}, 93.1 kg P ha^{-1}, and 53.8 kg K ha^{-1} in April 2022. Prior to planting, 134.5 kg N ha^{-1} of anhydrous ammonia was injected into the soil on 7 May 2022. Maize was planted on 10 May 2022. Finally, 32% urea-ammonium-nitrate (UAN) was Y-dropped as side-dressing (i.e., UAN liquid was injected on one side of each crop row) at 90.2 kg N ha^{-1} with ammonium thiosulfate at 13.2 kg N ha^{-1} on 11 June 2022. *Z. mays* was harvested on 28 October 2022. The soil in the field is roughly 70% Drummer silty clay loam and 30% Millbrook silt loam (Soil Survey Team; USDA-NRCS, 2023). In this region, the mean annual air temperature is 10°C, with a maximum monthly mean temperature of 24.4°C in July and a minimum of −5.5°C in January (Midwestern

Regional Climate Center). The mean annual precipitation is 1,008 mm, of which most rainfalls occur during the period of May to July (Illinois-Climate-Network, 2017).

To capture spatial and temporal variability in soil N_2O emissions at the field scale, net soil-atmosphere fluxes of N_2O were measured hourly using automated chambers at 16 locations in the maize field. The chambers were distributed among four sampling nodes (named Node 1–4) within a ~5 ha area of the field, with nodes 50–100 m distance apart. The node locations were selected to represent variation in temporal patterns in emissions measured manually in the 2021 growing season (Kim et al., 2024). Moreover, soil organic matter (SOM), pH, and topographic position varied among the four nodes, as measured in 2021 (Table S1 in Supporting Information S1). At each node, four automated chambers (LI-8200-104, LI-COR Biosciences, Lincoln, NE, USA) were radially installed at 12 m distance from a N_2O gas analyzer (LI-7820, LI-COR Biosciences, Lincoln, NE, USA) that sequentially measured hourly net soil-atmosphere N_2O fluxes from each chamber continuously with an automated gas sampling multiplexer (LI-8250, LI-COR Biosciences, Lincoln, NE, USA). Chambers were numbered Chamber 1–4 based on their clockwise position around the node's center. When referencing a chamber at a specific node we use to following shorthand: Chamber 4 at Node 2 = N2C4, and so forth. Chamber collars (20 cm diameter) were permanently installed directly adjacent from the crop row, allowing the chambers to be oriented such that the chamber top did not shade the crops or the collar footprint when the chambers were fully open between measurements. There was no vegetation between the crop rows and therefore no vegetation in the chamber footprint. Measurements continued from May 2022 until April 2023, excluding a ~3-week period in October–November 2022 during crop harvest and shorter outages for instrument maintenance or repair. The data sets were not gap-filled for this study. Using SoilFluxPro version 5.2.0 (LI-COR Biosciences, Lincoln, NE, USA), N_2O fluxes were calculated from an exponential fit applied to the change in N_2O concentration in the headspace from 30 to 490 s of the measurement period (total period 520 s). If the modeled exponential fit for a given flux measurement had an R^2 of <0.6, then data were visually inspected for evidence of bad chamber closure (e.g., non-monotonic fluctuations in the N2O concentration over time), which warranted exclusion of the flux measurement from the data set. Excluded flux data represented <0.03% of the total data set.

2.2. Comparison of Hot Moment Identification Approaches

We compared three outlier detection methods (2 SD or 4 SD, 1.5x IQR, and IF) on whole year data sets and seasonally subdivided data sets to determine how the hot moment identification approaches affected the hot moment threshold values, the percentage of hot moment contributions to annual or seasonal N_2O emissions, and the percentage of time in the year or season attributed to hot moments. The year was divided into three seasons: the early growing season (May 13–July 7, 2022) when hot moments were driven by fertilizer inputs, the late growing season (July 8–October 30, 2022) when hot moments were driven by rain events, and the non-growing season when hot moments were driven by freeze-thaw events (November 1, 2022–April 9, 2023). The breakpoints between the seasons were visually determined from plotting the whole year data sets for the 16 autochambers together (Figure S1 in Supporting Information S1).

We ran each of the outlier detection methods for the whole year and by individual season for each of the 16 autochambers. For the SD method, we calculated the mean and SD of the data set and then determined the hot moment threshold value as either two SD or four SD above the mean. For the 1.5x IQR method, the IQR is calculated as the difference between the 75th percentile (Q3) and the 25th percentile (Q1) of the data set. To identify the hot moment threshold, we calculated the upper threshold, which is Q3 plus 1.5 times the IQR. The IF method isolates anomalies instead of profiling normal data points. The algorithm utilizes 'isolation trees' to partition the data space, where anomalies are identified based on shorter path lengths in these trees, indicating easier isolation compared to normal points. For IF, we employed the IsolationForest function from sklearn. ensemble module in Python (version 3.10), setting the contamination parameter to 'auto'. This configuration allows the algorithm to automatically estimate the proportion of outliers in the data set. This approach classifies data points with an anomaly score below 0 as anomalies. The threshold for identifying significant hot moments in N_2O flux was determined by the lowest net N_2O flux value that corresponded to an anomaly score below this threshold.

Although all 16 autochamber data sets were right-skewed (Figure S2 in Supporting Information S1), for several reasons we chose not to transform the data sets to achieve normal distributions. First, about 4% of the net N_2O flux measurements across all data sets were negative fluxes that would have to be excluded to proceed with log transformation. Second, log transformation would diminish the data points on the high end of the frequency distributions such that the hot moment identification methods would not capture these extreme values as "hot moments." Third, IF is an unsupervised learning algorithm that does not assume a specific distribution, negating the need for transformation.

Using the determined threshold values above which a data point was considered part of a hot moment, we calculated the cumulative hot moment N_2O emissions and the number of hot moment data points. We calculated the percentage of hot moment contributions to cumulative N_2O emissions from the cumulative hot moment N_2O emissions divided by cumulative N_2O emissions. We also calculated the percentage of time in hot moments from the number of hot moment data points divided by the total number of N_2O flux data points. These calculations were performed separately for each of the 16 autochambers across the whole year and by individual season.

2.3. Statistical Analyses

We used one-way ANOVAs and Tukey pairwise comparisons to determine the effect of outlier detection method on threshold values, percentage of hot moment contributions to the cumulative N_2O emissions, and the percentage of time in hot moments in the whole year and in individual seasons. We also conducted similar analyses within each outlier detection method to determine the effect of season. Additionally, we calculated Pearson's coefficient of skew using the median for each autochamber's N_2O flux measurements. The 16 autochambers were considered independent replicates for this analysis because of the high variation among autochamber data sets, even within sampling nodes. This analysis was performed separately for the whole year data sets and for each of the three individual season data sets. These statistical analyses were performed in RStudio (version 4.2.2 (2022-10-31) —"Innocent and Trusting" © 2022 The R Foundation for Statistical Computing; Team, R 2019). Statistical significance was determined as $P < 0.05$.

3. Results

3.1. Comparison of Hot Moment Threshold Values

On average across all 16 autochamber data sets, the SD method yielded 1–2 orders of magnitude higher threshold values compared to the 1.5x IQR and IF methods, which had comparably lower threshold values (Table 1). The 4 SD method threshold values were significantly higher than the other two methods when considering the whole year and individual seasons (Table 1). This difference was detectable despite high variation in threshold values among autochambers: for the whole year analysis, thresholds ranged from 0.39–2.2, 0.0002–2.2, and 3.7–36 nmol $N_2O\ m^{-2}\ s^{-1}$ for 1.5x IQR, IF, and 4 SD methods, respectively (Figure S3 in Supporting Information S1). When the SD method was applied using 2 SD, the threshold values were still higher than for the 1.5x IQR and IF methods but due to large variance, these differences were statistically significant only for the comparison with the IF method for the whole year and late growing season (Table 1).

When subdividing the data sets into the early, late, and non-growing seasons, the threshold values determined by a given outlier detection method differed significantly among seasons (Table 1, Figure S3 in Supporting Information S1). All three methods yielded higher threshold values in the early growing season compared to the other two seasons, although for the IF method this was not statistically significant for the early versus non-growing season comparison (Table 1, Figures S4 and S5 in Supporting Information S1). Seasonally subdividing the data sets led to significantly increased and borderline significantly increased early growing season hot moment thresholds compared to whole year thresholds for the 1.5x IQR method and the SD methods, respectively, whereas it did not significantly decrease the late- and non-growing season thresholds relative to the whole year thresholds for these methods. In contrast, seasonally subdividing the data sets led to significantly and borderline significantly decreased late- and non-growing season thresholds, respectively, compared to whole year thresholds for the IF method, and it did not change the early season threshold relative to the whole year threshold (Table 1).

3.2. Comparison of Hot Moment Contributions to Cumulative N_2O Emissions

For the whole year and each season, the percentage of cumulative N_2O emissions from each chamber that was attributed to hot moments was, on average, lowest for the SD method applied as 2 SD or 4 SD compared to the other two outlier detection methods (Table S2, Figure S6 in Supporting Information S1). However, this pattern did not necessarily hold when comparing the three methods for a given chamber within an individual season

Table 1
Mean ± SE Net N_2O Flux Threshold Values (nmol N_2O m^{-2} s^{-1}) for the Four Hot Moment Outlier Detection Methods Applied to Whole Year Data Sets and Seasonally Subdivided Data Sets (N = 16 in All Cases)

	Outlier detection method				Compare by method
	1.5x IQR	Isolation forest	2 SD	4 SD	ANOVA main effects
Time interval					
Whole year	1.5 ± 0.24 (**ab, A**)	0.89 ± 0.14 (**b, B**)	5.3 ± 4.4 (**a, AB**)	9.9 ± 2.0 (**c, AB**)	$P < 0.001$, $F = 12$ ***
Early growing season	5.0 ± 0.90 (**a, B**)	0.92 ± 0.36 (**a, B**)	10 ± 10 (**ab, A**)	19 ± 4.6 (**b, B**)	$P < 0.001$, $F = 8.2$ ***
Late growing season	1.3 ± 0.44 (**ab, A**)	0.07 ± 0.03 (**a, A**)	2.2 ± 1.9 (**bc, B**)	3.9 ± 0.83 (**c, A**)	$P < 0.001$, $F = 9.1$ ***
Non-growing season	0.91 ± 0.28 (**a, A**)	0.34 ± 0.07 (**a, AB**)	1.5 ± 1.5 (**ab, B**)	2.7 ± 0.66 (**b, A**)	$P = 0.0013$, $F = 5.9$**
Compare by time interval					
ANOVA main effects	$P < 0.001$, $F = 13$ ***	$P = 0.01$, $F = 4.6$ *	$P < 0.001$, $F = 8.4$ ***	$P < 0.001$, $F = 8.1$ ***	

Note. Different lowercase letters indicate statistically significant Tukey pairwise differences among the outlier detection methods within a time interval (e.g., compare means across each time interval row). Different uppercase letters indicate statistically significant Tukey pairwise differences among the time intervals for each outlier detection method (e.g., compare means down each threshold method column). The column of ANOVA main effects corresponds to the differences among outlier detection methods, and the row of ANOVA main effects corresponds to the differences among seasons for a given method. For all one-way ANOVAs, df = 2. For $P < 0.001$, ***; $P < 0.01$ **; $P < 0.05$, *. To see all threshold values and summary boxplots for each autochamber by method and season, see Figures S3 and S4 in Supporting Information S1

(Figure 1). In the early growing season, the three methods were sometimes indistinguishable. For example, regardless of the outlier detection method, 99%–100% of the cumulative seasonal N_2O emissions was attributed to hot moments for the five autochambers with the highest cumulative early season N_2O emissions (N1C3, N1C4, N4C1, N4C2, and N4C3; Figure 1). For one chamber (N3C2), the IF method attributed 100% of cumulative seasonal N_2O emissions to hot moments in all three seasons, which was far higher than the other two methods.

For all outlier detection methods, the mean percentage of cumulative seasonal N_2O emissions attributed to hot moments was greater in the early growing season compared to the late and non-growing seasons (Figure 2, Table S2 in Supporting Information S1). However, this pattern did not necessarily hold across all chambers (Figure 1). For example, in Node 2, for Chambers 1 and 3, most of the cumulative annual flux was attributed to the non-growing season, but for Chambers 2 and 4 the cumulative N_2O flux was more evenly distributed among the seasons (Figure 1).

The percentage of time attributed to hot moments was higher for whole year data sets compared to the sum of seasonally subdivided data sets for the 1.5x IQR and SD methods but was the opposite for the IF method (Figure 2, Table S2 in Supporting Information S1). The hot moment contributions for 1.5x IQR, IF, 2 SD, and 4

Table 2
Mean Percentage (%) of Time for Each Season That was Identified as a Hot Moment Using the Different Outlier Detection Methods, Averaged Across All Chambers (n = 16 in All Cases); ± Corresponds to 1 SE From the Mean, and Letters Correspond to Tukey Pairwise Differences

	Outlier detection method				Compare by method
	1.5x IQR	Isolation forest	2 SD	4 SD	ANOVA main effects
Time interval					
Early growing season	9.3 ± 1.0 (**a, A**)	65 ± 9.7 (**b, B**)	4.2 ± 1.9 (**a, A**)	0.81 ± 0.11 (**a, A**)	$P < 0.001$, $F = 39$ ***
Late growing season	7.7 ± 1.2 (**a, A**)	89 ± 7.2 (**b, B**)	3.9 ± 1.2 (**a, A**)	0.85 ± 0.15 (**a, A**)	$P < 0.001$, $F = 136$ ***
Non-growing season	8.8 ± 0.58 (**a, A**)	23 ± 5.3 (**b, A**)	3.8 ± 1.1 (**a, A**)	1.2 ± 0.07 (**a, A**)	$P < 0.001$, $F = 13$ ***
Compare by time interval					
ANOVA main effects	$P = 0.51$, $F = 0.70$	$P < 0.001$, $F = 19$ ***	$P = 0.79$, $F = 0.23$	$P = 0.08$, $F = 2.7$	

Note. Different lowercase letters indicate statistically significant Tukey pairwise differences among the outlier detection methods within a time interval (e.g., compare means across each time interval row). Different uppercase letters indicate statistically significant Tukey pairwise differences among the time intervals for each outlier detection method (e.g., compare means down each threshold method column). The column of ANOVA main effects corresponds to the differences among outlier detection methods, and the row of ANOVA main effects corresponds to the differences among time intervals within a method. For all one-way ANOVAs, df = 2. For $P < 0.001$, ***, $P < 0.01$ **, $P < 0.05$, *.

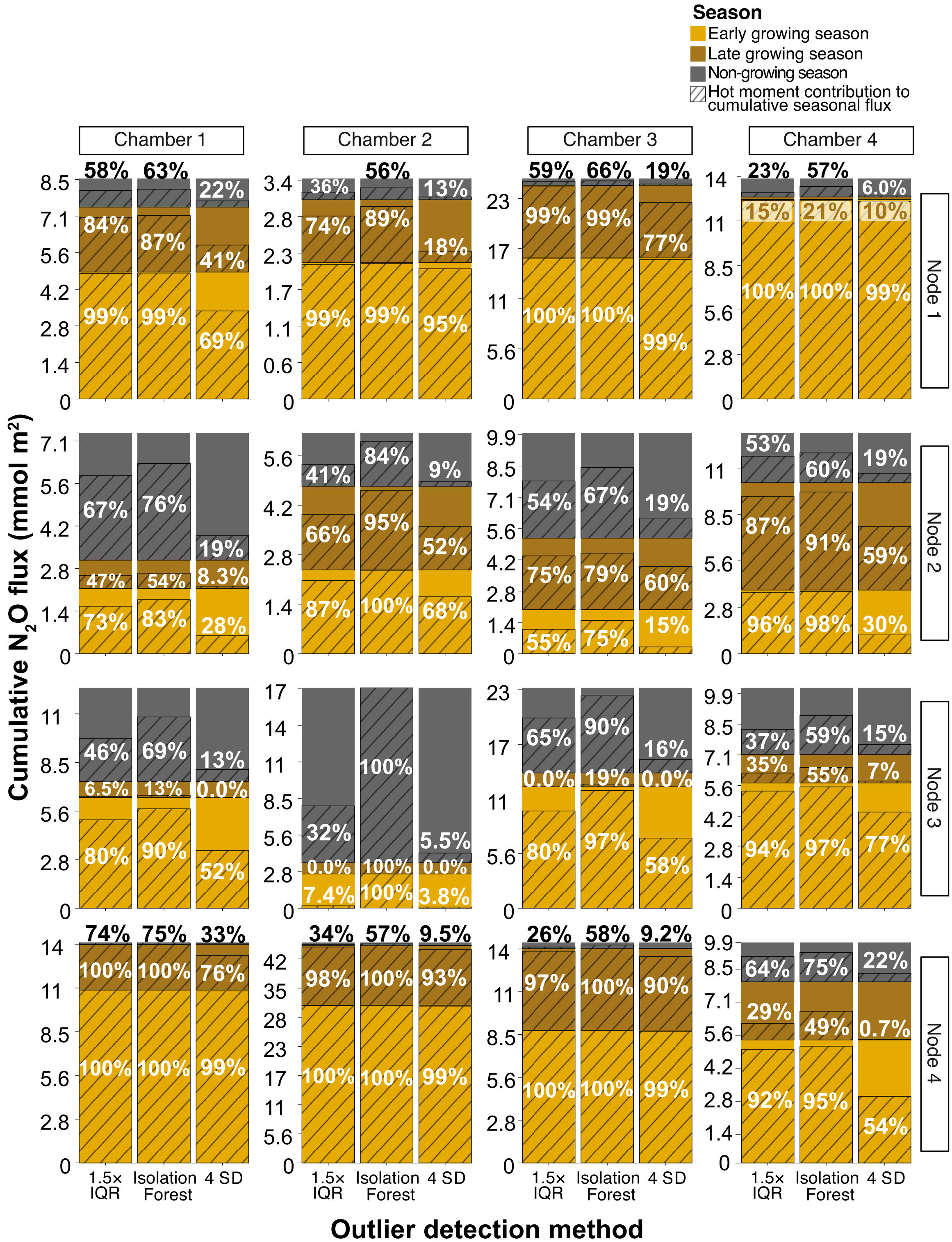

Figure 1. Hot moment contributions to the cumulative N_2O flux for each automated chamber over the whole sampling period (May 2022–April 2023). For each automated chamber (each panel in the figure), the three bars correspond to three outlier detection methods, the different color portions within each bar correspond to a different season, and the shaded fraction of each colored portion corresponds to the N_2O flux values that were included in hot moments. Flux values greater than or equal to the threshold value were considered part of a hot moment. The percentage values written inside each colored bar portion corresponds to the percentage of the N_2O flux for each season that was attributed to hot moments of N_2O.

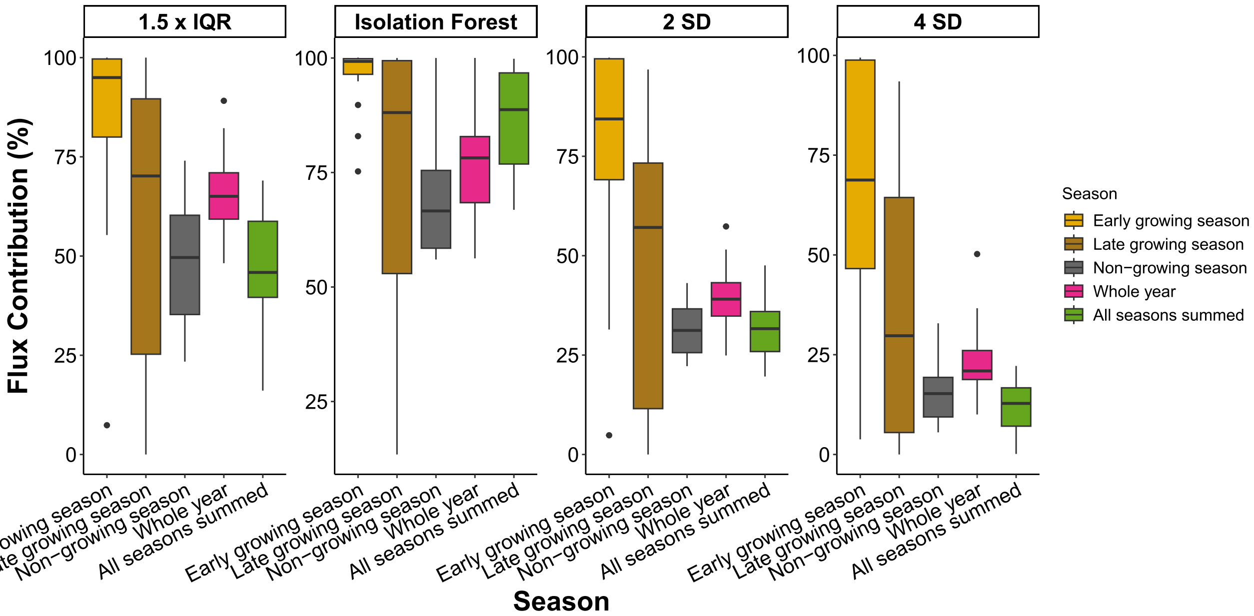

Figure 2. Mean ± SE hot moment contribution percentages (%) for the four hot moment outlier detection methods applied to the seasonal, whole year, and sum of seasons' hot moment contribution percentages data sets ($n = 16$ in all cases). One-way ANOVAs and Tukey pairwise comparisons were conducted among the time intervals for each outlier detection method (e.g., compare means within each panel), and among the outlier detection methods within a time interval (e.g., compare same color bars across panels). Details of all statistical analyses are included in Table S2 in Supporting Information S1.

SD differed by 19%, 9%, 8%, and 12%, respectively, for the summed seasonal contributions versus the whole year contributions (Figure 2, Table S2 in Supporting Information S1). Chamber by chamber, there was some more notable variation between the two approaches, but not across all chambers. Chambers that varied by 20% or more between the seasonally summed versus whole year hot moment contributions included: all Node 1 chambers, N3C1 and N4C3 for 1.5x IQR, N2C2, N2C4, and N4C4 for IF, and N4C1 and N4C2 for 4 SD (Figure S6 in Supporting Information S1).

3.3. Comparison of the Amount of Time Attributed to Hot Moments

The percentage of time within each season attributed to hot moments was significantly lower for the SD and 1.5x IQR methods compared to the IF outlier detection method (Table 2, Figure S7 in Supporting Information S1). Within each season, roughly 1%, 4%, and 9% of data points were categorized as hot moments by the 4 SD, 2 SD, and 1.5x IQR methods, respectively. Among seasons, the 1.5x IQR and SD methods attributed similar percentages of time to hot moments. In contrast, on average across all 16 autochambers, the IF method led to a highly variable percentage of time attributed to hot moments, ranging from 23% in the non-growing season to 89% in the late growing season. In addition, IF attributed higher percentages of time to hot moments during the early and late growing seasons, but a much lower percentage of time to hot moments during the non-growing season (Table 2, Figure S7 in Supporting Information S1).

4. Discussion

To better measure and mitigate N_2O emissions, we must first be able to identify and quantify hot moments of N_2O since they contribute disproportionately to annual N_2O budgets. Currently, there is no standard approach for hot moment identification, which challenges synthesis of knowledge about N_2O hot moments across studies. The work we present here is the first assessment of different approaches for hot moment identification and their implications for hot moment quantification.

Our analysis of 16 hourly net N_2O flux data sets that vary in N_2O flux magnitude and distribution revealed that the SD method yielded hot moment threshold values too high, and the IF method yielded threshold values too low (Table 1). This led to missed N_2O hot moments or low net N_2O fluxes mischaracterized as hot moments, respectively (Figures S3 and S4 in Supporting Information S1, Figure 1). Reducing the stringency of the SD method from 4 SD to 2 SD roughly halved the hot moment threshold values, but this still led to significantly lower hot moment contribution to cumulative N_2O emissions compared to both the 1.5x IQR and IF methods (Table S2 in Supporting Information S1). Hot moment identification by the 1.5x IQR method was most consistent with the qualitative definition of N_2O hot moments, yielding an estimate that on average 9% of the net hourly N_2O fluxes measured over the year were hot moments that contributed 66% of the cumulative N_2O emissions (Table 2, Table S2 in Supporting Information S1).

Seasonally subdividing the annual data sets facilitated identification of smaller hot moments in the late and non-growing seasons when N_2O hot moments were generally smaller (Table S2, Figures S4 and S5 in Supporting Information S1, Figure 1). However, it also increased the SD and 1.5x IQR hot moment threshold values in the early growing season when N_2O hot moments were larger, leading to lower estimates of hot moment contributions to annual N_2O emissions (Table 1, Figure S6 in Supporting Information S1). In the case of chambers N4C1 and N4C2, for 4 SD the seasonally summed hot moment contributions were substantially lower than for the whole year analysis because of particularly extreme early season hot moments that carried extra weight within early season analysis compared to whole season analysis. This led to both increased standard deviation and mean to elevate the threshold for hot moment identification in the early season analysis, excluding moderately high N_2O emissions from the estimates of hot moment contributions. In the case of specific chambers for 1.5x IQR and IF that also had substantial difference between seasonally summed versus whole year hot moment contributions, the distinguishing features of the magnitude and frequency distribution that led to this were unclear. In the interest of identifying the N_2O hot moments that are most important to measure and mitigate, we recommend whole year analyses as opposed to seasonally subdivided analyses.

4.1. Evaluation of Hot Moment Outlier Detection Methods

Our analysis suggests that the 4 SD method was too stringent for hot moment identification; the method misses what would reasonably be considered hot moments in visual evaluations of the 16 autochamber data sets (Figure S8 in Supporting Information S1). By definition, this method should only identify the top 0.1% of the net N_2O flux data as hot moments in data sets exhibiting normal distributions. When we applied the 4 SD method to untransformed right-skewed data sets, approximately 1% of the net N_2O flux data were identified as hot moments (Table 2, Figure S7 in Supporting Information S1). On average across the 16 autochamber data sets, the 4 SD method yielded 10 times higher hot moment threshold values which led to three times lower estimates of hot moment contributions to annual N_2O emissions compared to the 1.5x IQR and IF methods (Table 1 and Figure 1). The high threshold values estimated by the 4 SD method not only caused smaller hot moments to be missed but also caused net N_2O fluxes on the rising and falling limbs of large hot moment pulses to be missed (Figure S8 in Supporting Information S1). An exception to this stark difference between methods was the autochamber data sets that included extremely high N_2O fluxes following fertilization, which led to comparably high early growing season hot moment contributions (99%–100%) estimated by all four methods (Figures 1 and 2, Table S2 in Supporting Information S1). Relaxing the stringency of the SD method from 4 SD to 2 SD led to a ~50% reduction in the hot moment threshold values but these were still higher than values estimated from the 1.5x IQR and IF methods. Our analysis suggests that the SD method would not capture the importance of the smaller-magnitude hot moments to cumulative annual N_2O budgets because the threshold value is highly sensitive to the magnitude of the outlier flux values. We conclude that the SD method is appropriate only when used on flux data sets with normal distributions, regardless of the stringency with which it is applied.

The 1.5x IQR and IF methods yielded similar estimates of hot moment contributions to annual or seasonal N_2O emissions (Figure 1, Figure S6 in Supporting Information S1), but the IF method often attributed considerably more net N_2O flux data to hot moments (Figure S7 in Supporting Information S1, Table 2). This was due to lower hot moment threshold values estimated by the IF method which led to more N_2O flux data points attributed to hot moments (Table 1, Figures S3 and S4 in Supporting Information S1). However, these smaller "N_2O hot moments" contributed little to cumulative N_2O emissions over the year or the individual season (Figures S3, S4 and S5 in Supporting Information S1, Figure 1). This was most exaggerated in the late growing season, which was marked by few and small hot moments across most autochambers. On average across the 16 autochamber data sets, the late growing season threshold value estimated by the IF method was so low (10 times lower than that estimated by the 1.5x IQR method), that 89% of late growing season net N_2O flux data points were attributed to hot moments (Figures S4, S5 in Supporting Information S1, Figure 2, Table S2 in Supporting Information S1). Even in the early growing season when large hot moments occurred, the IF method on average attributed 65% of net N_2O flux data points to hot moments (Figure 2, Table S2 in Supporting Information S1). The IF method, therefore, appears too permissive in identifying N_2O hot moments, which should represent short periods of high net N_2O fluxes that disproportionately contribute to cumulative N_2O emissions (Wagner-Riddle et al., 2020). We used the IF method with the contamination factor set on "auto," which allows the machine-learning algorithm to determine the percentage of net N_2O fluxes that are anomalous as opposed to setting the contamination factor to a fixed value that would determine this percentage. In contrast, the percentage of net N_2O fluxes attributed to hot moments by the 1.5x IQR method was constrained to ∼9%, which is more in line with the qualitative definition of hot moments that suggests that hot moments should account for far less than 50% of the measured net N_2O fluxes (Table 2, Figure S7 in Supporting Information S1; Wagner-Riddle et al., 2020). As the flux distribution becomes more right-skewed, this percentage of N_2O fluxes identified as hot moments will become greater even though the calculation of the hot moment threshold value is robust against non-normal distributions. We conclude that, of the three outlier detection methods we evaluated, the 1.5x IQR method strikes the best balance in identifying hot moments based on the qualitative criteria regarding the proportion of a time series attributed to hot moments and the magnitude of the emissions. Moreover, the 1.5x IQR method is the least sensitive to flux magnitude and distribution out of the three outlier detection methods that we evaluated, suggesting that it could be applied in a standardized manner across data sets.

4.2. Evaluation of Whole Year Versus Seasonally Subdivided Analyses

Because different mechanisms trigger different magnitude N_2O hot moments in the different seasons, we evaluated seasonally subdivided N_2O flux data sets to ensure that hot moments were appropriately identified in all seasons. Although most of the 16 autochamber data sets exhibited large N_2O hot moments in the early growing season and smaller N_2O hot moments in the late- and non-growing seasons (Figure 1, Figure S8 in Supporting Information S1), the threshold values estimated from the analysis of whole year data sets did not exclude the smaller N_2O hot moments (Table 1). As such, seasonally subdividing the data sets was not necessary to improve hot moment identification. On the contrary, it detrimentally affected hot moment identification in the early growing season by raising the hot moment threshold value estimated by the SD and 1.5x IQR methods (Table 1). This resulted in a decrease in estimated hot moment contributions to annual N_2O emissions (Figures 1 and 2, Table S2 in Supporting Information S1). For the IF method, the low threshold values estimated for the late- and non-growing seasons led to more than half of those seasons being inappropriately identified as hot moments, thereby increasing the estimated hot moment contribution to annual N_2O emissions relative to whole year analysis (Figure 1). We conclude that seasonal subdivision of N_2O flux data sets can be counterproductive to N_2O hot moment identification and quantification regardless of the outlier detection method.

Conflict of Interest

The authors declare no conflicts of interest relevant to this study.

Data Availability Statement

All code and data necessary to reproduce our results are available in our online GitHub repository (https://github.com/jiacheng-x/N2O-analysis) and permanently archived at the Illinois Data Bank (https://doi.org/10.13012/B2IDB-8414089_V1, Stuchiner et al., 2024).

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