

1 **Hot or not? An evaluation of methods for identifying hot moments**
2 **of nitrous oxide emissions from soils**

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23 Open access: We have uploaded all finalized data to www.scholar.colorado.edu Accession
24 number forthcoming. In the meantime, data are available upon request.

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47 **Abstract**

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49 Effectively quantifying hot moments of nitrous oxide (N₂O) emissions from agricultural soils is
50 critical for managing this potent greenhouse gas. However, we are challenged by a lack of
51 standard approaches for identifying hot moments, including (1) determining thresholds above
52 which emissions are considered hot moments, and (2) considering seasonal variation in the
53 magnitude and frequency distribution of net N₂O fluxes. We used one year of hourly N₂O flux
54 measurements from 16 autochambers that varied in flux magnitude and frequency distribution in
55 a conventionally tilled maize field in central Illinois, USA to compare three approaches to
56 identify hot moment thresholds: 4x the standard deviation (SD) above the mean, 1.5x the
57 interquartile range (IQR), and isolation forest (IF) identification of anomalous values. We also
58 compared these approaches on seasonally subdivided data (early, late, non-growing seasons) vs.
59 the whole year. Our analyses of the datasets revealed that 1.5x IQR method best identified N₂O
60 hot moments. In contrast, the 4 SD method yielded hot moment threshold values too high, and
61 the IF method yielded threshold values too low, leading to missed N₂O hot moments or low net
62 N₂O fluxes mischaracterized as hot moments, respectively. Furthermore, seasonally subdividing
63 the dataset facilitated identification of smaller hot moments in the late and non-growing seasons
64 when N₂O hot moments were generally smaller, but it also increased hot moment threshold
65 values in the early growing season when N₂O hot moments were larger. Consequently, we
66 recommend using the 1.5x IQR method on whole year datasets to identify N₂O hot moments.

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70 **Plain Language Summary**

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72 Nitrous oxide (N₂O) is a greenhouse gas that traps 273 times more heat in Earth's
73 atmosphere than carbon dioxide (CO₂) on a per molecule basis. Microbes in the soil produce
74 N₂O, with short bursts of high production stimulated by environmental triggers such as rainfall
75 or fertilization. Management strategies targeting these brief periods of high N₂O production can
76 be particularly effective in reducing cumulative annual soil N₂O emissions from agricultural
77 fields. However, to date there is no standard approach to identifying hot moments. Here, we
78 analyzed 16 one-year datasets of hourly N₂O emission measurements from a large area in one
79 maize field to compared different methods that are used to identify hot moments of N₂O. We
80 learned that the threshold values above which N₂O emissions would be considered hot moments
81 were best determined as 1.5 times greater than the N₂O emission value that fell in the middle of
82 all the emission values in the dataset, a method called "1.5x the interquartile range." We could
83 also best identify hot moments of N₂O when we analyzed the whole year N₂O datasets as
84 opposed to seasonally subdividing the datasets. Our recommendations to standardize N₂O hot
85 moment identification will facilitate synthesis of knowledge across studies.

86

87 **Introduction**

88

89 Nitrous oxide (N₂O) currently accounts for 6% of Earth's radiative forcing (Dutton et al.
90 2023), and soil emissions contribute significantly to rising atmospheric concentrations of this
91 potent greenhouse gas. Soil N₂O emissions are often characterized by short periods of high
92 reaction rates that contribute disproportionately to cumulative annual N₂O emissions, referred to

93 as hot moments (Groffman et al. 2009, Bernhart et al. 2015, Wagner-Riddle et al. 2020). Hot
94 moments are prime targets for land management practices to mitigate N₂O emissions, especially
95 in agroecosystems (Wagner-Riddle et al. 2020). However, there is high uncertainty in the
96 effectiveness of agricultural land management practices in reducing emissions, in part because
97 assessments largely rely on relatively infrequent manual chamber-based emissions measurements
98 that may miss many of the hot moments (Kravchenko and Robertson 2015, Charteris et al. 2020).
99 Understanding of N₂O hot moments from high temporal resolution datasets derived from
100 autochamber and micrometeorological measurements can help guide improved manual chamber
101 measurement sampling to better capture hot moments (Tallec et al. 2019, Lawrence et al. 2021,
102 Anthony and Silver 2021) and parameterize models to more accurately predict N₂O budgets on
103 regional to global scales (O’Connell et al. 2022). Despite these datasets becoming more common
104 (Charteris et al. 2020, Dorrich et al. 2020), there currently is no standard approach for hot
105 moment identification, and the implications of different approaches on hot moment identification
106 and quantification have not previously been evaluated.

107 There are several methods for identifying N₂O hot moments, wherein emission values
108 above a threshold are considered part of an N₂O hot moment (Bernhart et al. 2015). Often,
109 thresholds are arbitrarily determined when visualizing the time series of net N₂O flux data
110 (Mander et al. 2021, Rautakoski et al. 2023). Statistical methods can be applied in a more
111 standardized manner across studies, but the threshold values determined depend on the frequency
112 distribution of individual N₂O flux datasets. For example, assuming a dataset is normally
113 distributed, using 1.5x the interquartile range (1.5x IQR; e.g., Molodovskaya et al. 2012) of the
114 measured net N₂O fluxes, flux values higher than 99.3% of the distribution are considered part of
115 N₂O hot moments. Using four standard deviations (4 SD) above the mean (e.g., Anthony and

116 Silver 2021), only flux values in the top 0.1% of the distribution are identified as hot moments.
117 These statistical methods are grounded in the assumption that datasets are normally distributed;
118 however, this assumption belies the very behavior of N₂O hot moments (episodic and large
119 emission pulses), which typically leads to right skewed N₂O flux datasets. Transforming the
120 datasets to achieve normal distributions can lead to extremely high threshold values that result in
121 few identified hot moments, particularly using the 4 SD method. Consequently, distribution-free
122 methods such as isolation forest (IF) classification, which are free of assumptions about the
123 shape of the probability distribution of a dataset, could be more appropriate for hot moment
124 identification (Ackett et al. 2022). Isolation forest (IF) classification is a machine-learning
125 method that uses binary trees to identify anomalous data points based on short path-lengths in the
126 trees that indicate that the data points are few and different from the rest of the dataset. These
127 threshold determination methods have not been compared across N₂O flux datasets that vary in
128 flux magnitude and distribution, leaving uncertain how much the methods can differ in hot
129 moment identification and the estimated fraction of annual N₂O emissions attributed to hot
130 moments.

131 Seasonal variation in N₂O flux magnitude and distribution could lead to bias in hot
132 moment identification and quantification when considering whole year datasets compared to
133 seasonally subdivided datasets. In agroecosystems, N₂O hot moments are largely governed by
134 seasonally distinct triggers (Butterbach-Bahl et al. 2013). In the early growing season
135 fertilization with ammonium (NH₄⁺) or nitrate (NO₃⁻) drives hot moments (Molodovskaya et al.
136 2012, Roy et al. 2014). Throughout the growing season, irrigation or rainfall drives hot moments
137 (Griffis et al. 2017, Song et al. 2021). During the winter and spring, freeze-thaw and thaw drive
138 hot moments, respectively (Risk et al. 2013, Wagner-Riddle et al. 2017). The flux magnitudes of

139 these hot moments vary, with fertilization-driven hot moments typically yielding larger-
140 magnitude N₂O fluxes than rainfall-driven hot moments (Kostyanovsky et al. 2019). Thaw-
141 related hot moments can be even larger but vary in magnitude depending on the strength of a
142 freeze event prior to thaw (Butterbach-Bahl et al. 2002, Groffman et al. 2009). Mitigating both
143 larger and smaller N₂O hot moments can potentially be important to reducing annual N₂O
144 emissions, with mitigation strategies targeting the different mechanisms responsible for N₂O hot
145 moments in different seasons. However, studies to date have conducted hot moment
146 identification on whole year datasets such that the larger fertilization and thaw-driven N₂O
147 emission pulses elevate the thresholds used to identify N₂O hot moments, causing the smaller,
148 more frequent hot moments from other seasons to be missed. Because seasonally subdivided hot
149 moment identification has not been previously conducted, it is not known how much these
150 smaller N₂O hot moments contribute to annual N₂O emissions.

151 Here, we evaluated different threshold determination methods on whole year and
152 seasonally subdivided net N₂O flux datasets to determine which approach best captured N₂O hot
153 moments across datasets varying in N₂O flux magnitude and distribution. We took advantage of a
154 unique study in which one year of hourly measurements of net N₂O flux were collected from 16
155 autochambers located in a ~5 ha area of a conventionally tilled maize field in central Illinois,
156 USA. The autochambers were placed to capture variation in N₂O dynamics, including consistent
157 N₂O cold spots and episodic N₂O hot spots (Zhang et al. 2023). The variation in N₂O flux
158 magnitude and distribution among the 16 autochamber datasets provided the opportunity to
159 robustly assess how hot moment identification using (1) the 4 SD, 1.5x IQR and IF methods, and
160 (2) whole year datasets versus seasonally subdivided datasets (early growing season, late
161 growing season, and non-growing season) affected hot moment threshold values and

162 quantification of N₂O hot moment fluxes. Based on our findings, we provide recommendations
163 to standardize hot moment identification approaches.

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165 **Methods**

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167 *Net N₂O flux data collection*

168 Net N₂O fluxes were measured in a commercial field located near Villa Grove, IL that
169 was cultivated in maize-maize-soy rotations with conventional tillage and planted with maize (*Z.*
170 *mays*) during the 2022 growing season. Deep chisel tillage was performed in November 2021.
171 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
172 ha⁻¹ in April 2022. Prior to planting, 134.5 kg N ha⁻¹ of anhydrous ammonia was injected into
173 the soil on May 7, 2022. Maize was planted on May 10, 2022. Finally, 32% UAN was Y-dropped
174 as side-dressing at 90.2 kg N ha⁻¹ with ammonium thiosulfate at 13.2 kg N ha⁻¹ on June 11,
175 2022. *Z. mays* was harvested on October 28, 2022. The soil in the field is roughly 70% Drummer
176 silty clay loam and 30% Millbrook silt loam (USDA-NRCS, 2022). In this region, the mean
177 annual air temperature is 10 °C, with a maximum monthly mean temperature of 24.4 °C in July
178 and a minimum of -5.5 °C in January (Midwestern Regional Climate Center). The mean annual
179 precipitation is 1008 mm, of which most rainfalls occur during the period of May to July
180 (Illinois-Climate-Network, 2017).

181 To capture spatial and temporal variability in soil N₂O emissions at the field scale, net
182 soil-atmosphere fluxes of N₂O were measured hourly using automated chambers at 16 locations
183 in the maize field. The chambers were distributed among four sampling nodes within a ~5 ha
184 area of the field. At each node, four automated chambers (LI-8200-104, LI-COR Biosciences,

185 Lincoln, NE, USA) were radially installed at 12 m distance from a N₂O gas analyzer (LI-7820,
186 LI-COR Biosciences, Lincoln, NE, USA) that sequentially measured hourly net soil-atmosphere
187 N₂O fluxes from each chamber continuously with an automated gas sampling multiplexer (LI-
188 8250, LI-COR Biosciences, Lincoln, NE, USA) starting in May 2022 until April 2023, excluding
189 a ~3-week period in October-November 2022 during crop harvest.

190

191 *Comparison of hot moment identification approaches*

192 We compared three threshold value determination methods (4 SD, 1.5x IQR, and IF) on
193 whole year datasets and seasonally subdivided datasets to determine how the hot moment
194 identification approaches affected the hot moment threshold values, the percentage of hot
195 moment contributions to annual or seasonal N₂O emissions, and the percentage of time in the
196 year or season attributed to hot moments. The year was divided into three seasons: the early
197 growing season (May 13-July 7, 2022) when hot moments were driven by fertilizer inputs, the
198 late growing season (July 8-October 30, 2022) when hot moments were driven by rain events,
199 and the non-growing season when hot moments were driven by freeze-thaw events (November 1,
200 2022-April 9, 2023). The breakpoints between the seasons were visually determined from
201 plotting the whole year datasets for the 16 autochambers together (Figure S1).

202 We ran each of the threshold value determination methods for the whole year and by
203 individual season for each of the 16 autochambers. For the 4 SD method, we calculated the mean
204 and SD of the dataset and then determined the hot moment threshold value as four SD above the
205 mean. For the 1.5x IQR method, the IQR is calculated as the difference between the 75th
206 percentile (Q3) and the 25th percentile (Q1) of the dataset. To identify the hot moment threshold,
207 we calculated the upper threshold, which is Q3 plus 1.5 times the IQR. The IF method isolates

208 anomalies instead of profiling normal data points. The algorithm utilizes 'isolation trees' to
209 partition the data space, where anomalies are identified based on shorter path lengths in these
210 trees, indicating easier isolation compared to normal points. For IF, we employed
211 the IsolationForest function from sklearn.ensemble module in Python (version 3.10), setting
212 the contamination parameter to 'auto'. This configuration allows the algorithm to automatically
213 estimate the proportion of outliers in the dataset. This approach classifies data points with an
214 anomaly score below 0 as anomalies. The threshold for identifying significant hot moments in
215 N₂O flux was determined by the lowest net N₂O flux value that corresponded to an anomaly
216 score below this threshold.

217 Although all 16 autochamber datasets were right-skewed (Figure S2), for several reasons
218 we chose not to transform the datasets to achieve normal distributions. First, about 4% of the net
219 N₂O flux measurements across all datasets were negative fluxes that would have to be excluded
220 to proceed with log transformation. Second, log transformation would diminish the data points
221 on the high end of the frequency distributions such that the hot moment identification methods
222 would not capture these extreme values as “hot moments.” Third, IF is an unsupervised learning
223 algorithm that does not assume a specific distribution, negating the need for transformation.

224 Using the determined threshold values above which a data point was considered part of a
225 hot moment, we calculated the cumulative hot moment N₂O emissions and the number of hot
226 moment data points. We calculated the percentage of hot moment contributions to cumulative
227 N₂O emissions from the cumulative hot moment N₂O emissions divided by cumulative N₂O
228 emissions. We also calculated the percentage of time in hot moments from the number of hot
229 moment data points divided by the total number of N₂O flux data points. These calculations were

230 performed separately for each of the 16 autochambers across the whole year and by individual
231 season.

232

233 *Statistical analyses*

234 We used one-way ANOVAs and Tukey pairwise comparisons to determine the effect of
235 threshold determination method on threshold values, percentage of hot moment contributions to
236 the cumulative N₂O emissions, and the percentage of time in hot moments in the whole year and
237 in individual seasons. We also conducted similar analyses within each threshold determination
238 method to determine the effect of season. Additionally, we calculated Pearson's coefficient of
239 skew using the median for each autochamber's N₂O flux measurements. The 16 autochambers
240 were considered independent replicates for this analysis because of the high variation among
241 autochamber datasets, even within sampling nodes. This analysis was performed separately for
242 the whole year datasets and for each of the three individual season datasets. These statistical
243 analyses were performed in RStudio (version 4.2.2 (2022-10-31) -- "Innocent and Trusting" ©
244 2022 The R Foundation for Statistical Computing). Statistical significance was determined as $P <$
245 0.05.

246

247 **Results**

248

249 *Comparison of hot moment threshold values*

250 On average across all 16 autochamber datasets, the 4 SD method yielded 1-2 orders of
251 magnitude higher threshold values compared to the 1.5x IQR and IF methods, which had
252 comparably lower threshold values (Table 1). The 4 SD method threshold values were

253 significantly higher than the other two methods when considering the whole year and individual
254 seasons (Table 1). This difference was detectable despite high variation in threshold values
255 among autochambers: for the whole year analysis, thresholds ranged from 0.39-2.2, 0.0002-2.2,
256 and 3.7-36 nmol N₂O m⁻² s⁻¹ for 1.5x IQR, IF, and 4 SD methods, respectively (Figure S3).

257 When subdividing the datasets into the early, late, and non-growing seasons, the
258 threshold values determined by a given threshold determination method differed significantly
259 among seasons (Table 1, Figure S3). All three methods yielded higher threshold values in the
260 early growing season compared to the other two seasons, although for the IF method this was not
261 statistically significant for the early versus non-growing season comparison (Table 1, Figure S4).
262 Seasonally subdividing the datasets led to increased early growing season hot moment thresholds
263 compared to whole year thresholds for the 1.5x IQR and 4 SD methods, whereas it did not
264 significantly decrease the late- and non-growing season thresholds relative to the whole year
265 thresholds. In contrast, seasonally subdividing the datasets led to decreased late- and non-
266 growing season thresholds compared to whole year thresholds for the IF method, and it did not
267 change the early season threshold relative to the whole year threshold.

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269

270 **Table 1.** Mean \pm SE net N₂O flux threshold values (nmol N₂O m⁻² s⁻¹) for the three hot moment threshold determination method applied to whole year datasets
 271 and seasonally subdivided datasets (N = 16 in all cases). Different lowercase letters indicate statistically significant Tukey pairwise differences at P < 0.05 among
 272 the threshold determination methods. Different uppercase letters indicate statistically significant Tukey pairwise differences at P < 0.05 among the time intervals
 273 for each threshold determination method. The column of ANOVA main effects corresponds to the differences among threshold determination methods, and the
 274 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
 275 **, P < 0.05, *. To see all threshold values for each autochamber by method and season, see Figures S3 and S4 in the Supplement.
 276

	Threshold determination method		Compare by method	
	1.5x IQR	Isolation forest	4 SD	ANOVA main effects
Time interval				
Whole year	1.5 \pm 0.24 (a, A)	0.89 \pm 0.14 (a, B)	9.9 \pm 2.0 (b, AB)	P < 0.001, F = 18 ***
Early growing season	5.0 \pm 0.90 (a, B)	0.92 \pm 0.36 (a, B)	19 \pm 4.6 (b, B)	P < 0.001, F = 12 ***
Late growing season	1.3 \pm 0.44 (a, A)	0.07 \pm 0.03 (a, A)	3.9 \pm 0.83 (b, A)	P < 0.001, F = 12 ***
Non-growing season	0.91 \pm 0.28 (a, A)	0.34 \pm 0.07 (a, AB)	2.7 \pm 0.66 (b, A)	P < 0.001, F = 8.4 ***
Compare by time interval				
ANOVA main effects	P < 0.001, F = 13 ***	P = 0.01, F = 4.6 *	P < 0.001, F = 8.1 ***	

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279 *Comparison of hot moment contributions to cumulative N₂O emissions*

280 For the whole year and each season, the percentage of cumulative N₂O emissions from
281 each chamber that was attributed to hot moments was, on average, lowest for the 4 SD method
282 compared to the other two threshold determination methods (Table 2). However, this pattern did
283 not necessarily hold when comparing the three methods for a given chamber within an individual
284 season (Figure 1). In the early growing season, the three methods were sometimes
285 indistinguishable. For example, regardless of the threshold determination method, 99-100% of
286 the cumulative seasonal N₂O emissions was attributed to hot moments for the five autochambers
287 with the highest cumulative early season N₂O emissions (N1C3, N1C4, N4C1, N4C2, N4C3;
288 Figure 1). For one chamber (N3C2), the IF method attributed 100% of cumulative seasonal N₂O
289 emissions to hot moments in all three seasons, which was far higher than the other two methods.

290 For all threshold determination methods, the mean percentage of cumulative seasonal
291 N₂O emissions attributed to hot moments was greater in the early growing season compared to
292 the late and non-growing seasons (Table 2). However, this pattern did not necessarily hold across
293 all chambers (Figure 1). For example, in Node 2, for Chambers 1 and 3, most of the cumulative
294 annual flux was attributed to the non-growing season, but for Chambers 2 and 4 the cumulative
295 N₂O flux is more evenly distributed among the seasons (Figure 1).

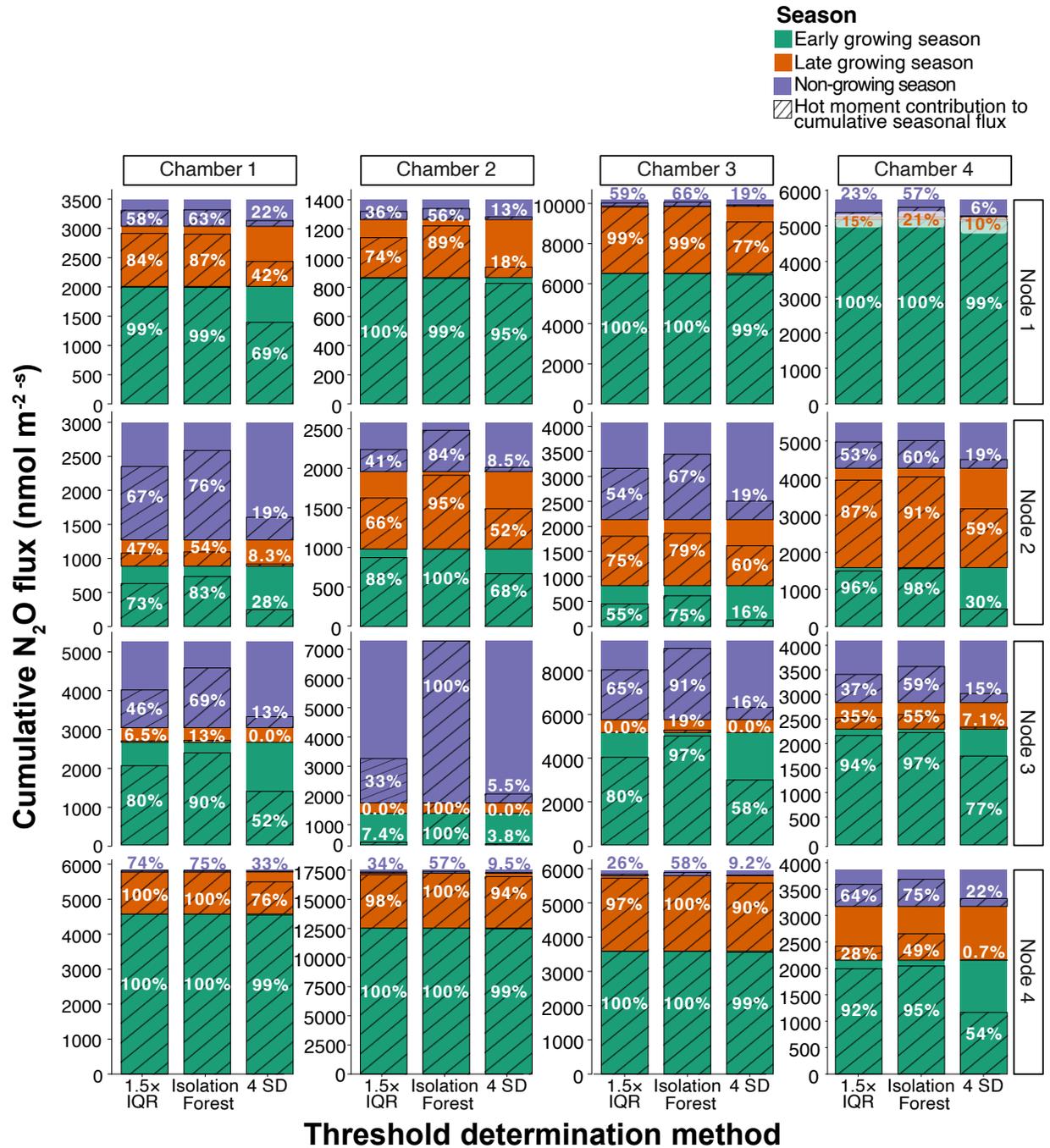
296 The percentage of time attributed to hot moments was higher for whole year datasets
297 compared to the sum of seasonally subdivided datasets for the 1.5x IQR and 4 SD methods but
298 was the opposite for the IF method (Table 2). The hot moment contributions for 1.5x IQR, IF,
299 and 4 SD differed by 19%, 9%, and 12%, respectively, for the summed seasonal contributions vs.
300 the whole year contributions (Table 2). Chamber by chamber, there was some more notable
301 variation between the two approaches, but not across all chambers. Chambers that varied by 20%

302 or more between the seasonally summed vs. whole year hot moment contributions included: all
303 Node 1 chambers, N3C1, and N4C3 for 1.5x IQR, N2C2, N2C4, and N4C4 for IF, and N4C1 and
304 N4C2 for 4 SD (Figure S5).

305 **Table 2.** Mean \pm SE hot moment contribution percentages (%) for the three hot moment threshold determination methods applied to whole year datasets and
 306 seasonal datasets (n = 16 in all cases). Different lowercase letters indicate statistically significant Tukey pairwise differences at $P < 0.05$ among the threshold
 307 determination methods. Different uppercase letters indicate statistically significant Tukey pairwise differences at $P < 0.05$ among the time intervals for each
 308 threshold determination method. The column of ANOVA main effects corresponds to the differences among threshold determination methods, and the first row of
 309 ANOVA main effects corresponds to the differences among seasons within a method. The second row of ANOVA main effects corresponds to the differences
 310 between the whole year versus the sum of individual seasons. For all one-way ANOVAs, $df = 2$. For $P < 0.001$, ***, $P < 0.01$ **, $P < 0.05$, *.

	Threshold determination method			Compare by method
	1.5x IQR	Isolation forest	4 SD	ANOVA main effects
Time interval				
Whole year	66 \pm 2.8 (b, AB)	76 \pm 2.9 (a, A)	24 \pm 2.3 (c, A)	$P < 0.001$, $F = 107$ ***
Early growing season	85 \pm 6.1 (ab, B)	96 \pm 1.8 (b, B)	65 \pm 8.2 (a, B)	$P = 0.003$, $F = 6.7$ **
Late growing season	57 \pm 9.4 (ab, A)	72 \pm 8.0 (b, A)	37 \pm 8.8 (a, A)	$P = 0.03$, $F = 4.0$ *
Non-growing season	48 \pm 3.9 (b, A)	70 \pm 3.3 (c, A)	16 \pm 1.8 (a, A)	$P < 0.001$, $F = 76$ ***
All seasons summed	47 \pm 3.5 (b, A)	87 \pm 3.0 (c, B)	12 \pm 2.3 (a, A)	$P < 0.001$, $F = 177$ ***
Compare by time interval				
ANOVA main effects	$P < 0.001$, $F = 6.7$ ***	$P < 0.001$, $F = 6.6$ **	$P < 0.001$, $F = 12$ ***	
	$P < 0.001$, $F = 18$ ***	$P = 0.02$, $F = 6.2$ *	$P < 0.001$, $F = 16$ ***	

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 314 **Figure 1.** Hot moment contributions to the cumulative N₂O flux for each automated chamber over the whole
 315 sampling period (May 2022-April 2023). For each automated chamber (each panel in the figure), the three bars
 316 correspond to the three threshold determination methods, the different color portions within each bar correspond to a
 317 different season, and the shaded fraction of each colored portion corresponds to the N₂O flux values that were
 318 included in hot moments. Flux values greater than or equal to the threshold value were considered part of a hot
 319 moment. The percentage values written inside each colored bar portion corresponds to the percentage of the N₂O
 320 flux for each season that was attributed to hot moments of N₂O.

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324 *Comparison of the amount of time attributed to hot moments*

325 The percentage of time within each season attributed to hot moments was significantly lower
326 for the 4 SD and 1.5x IQR methods compared to the IF threshold determination method (Table 3,
327 Figure S6). Within each season, roughly 1% and 9% of data points were categorized as hot
328 moments by the 4 SD and 1.5x IQR methods, respectively. Among seasons, the 1.5x IQR and 4
329 SD methods attributed similar percentages of time to hot moments. In contrast, on average across
330 all 16 autochambers, the IF method led to a highly variable percentage of time attributed to hot
331 moments, ranging from 23% in the non-growing season to 89% in the late growing season. In
332 addition, IF attributed higher percentages of time to hot moments during the early and late
333 growing seasons, but a much lower percentage of time to hot moments during the non-growing
334 season (Table 3, Figure S6).

335 **Table 3.** Mean percentage of time for each season that was identified as a hot moment using the different threshold determination methods, averaged across all
 336 chambers (n = 16 in all cases); ± corresponds to 1 SE from the mean, and letters correspond to Tukey pairwise differences. Different lowercase letters indicate
 337 statistically significant Tukey pairwise differences at P < 0.05 among the threshold determination methods. Different uppercase letters indicate statistically
 338 significant Tukey pairwise differences at P < 0.05 among the seasons for each threshold determination method. The column of ANOVA main effects corresponds
 339 to the differences among threshold determination methods, and the row of ANOVA main effects corresponds to the differences among seasons within a method.
 340 For all one-way ANOVAs, df = 2. For P < 0.001, ***, P < 0.01 **, P < 0.05, *.
 341

	Threshold determination method			Compare by method
	1.5x IQR	Isolation forest	4 SD	ANOVA main effects
Season				
Early growing season	9.3 ± 1.0 (a, A)	65 ± 9.7 (b, B)	0.81 ± 0.11 (a, A)	P < 0.001, F = 38 ***
Late growing season	7.7 ± 1.2 (b, A)	89 ± 7.2 (a, B)	0.85 ± 0.15 (b, A)	P < 0.001, F = 136 ***
Non-growing season	8.8 ± 0.58 (a, A)	23 ± 5.3 (b, A)	1.2 ± 0.07 (a, A)	P < 0.001, F = 13 ***
Compare by season				
ANOVA main effects	P = 0.51, F = 0.70	P < 0.001, F = 19 ***	P = 0.08, F = 2.7	

342

343 **Discussion**

344

345 To better measure and mitigate N₂O emissions, we must identify and quantify hot
346 moments of N₂O that contribute disproportionately to annual N₂O budgets. Currently, there is no
347 standard approach for hot moment identification, which challenges synthesis of knowledge about
348 N₂O hot moments across studies. The work we present here is the first assessment of different
349 approaches for hot moment identification and their implications for hot moment quantification.

350 Our analysis of 16 hourly net N₂O flux datasets that vary in N₂O flux magnitude and
351 distribution revealed that the 4 SD method yielded hot moment threshold values too high, and the
352 IF method yielded threshold values too low. This led to missed N₂O hot moments or low net N₂O
353 fluxes mischaracterized as hot moments, respectively (Table 1, Figure S3, Figure 1). Hot
354 moment identification by the 1.5x IQR method was most consistent with the definition of N₂O
355 hot moments, yielding an estimate that on average 9% of the net N₂O fluxes measured over the
356 year were hot moments that contributed 66% of the cumulative N₂O emissions (Table 3, Table
357 2). Seasonally subdividing the annual datasets facilitated identification of smaller hot moments
358 in the late and non-growing seasons when N₂O hot moments were generally smaller (Table 2,
359 Figure S4, Figure 1). However, it also increased the 4 SD and 1.5x IQR hot moment threshold
360 values in the early growing season when N₂O hot moments were larger, leading to lower
361 estimates of hot moment contributions to annual N₂O emissions (Table 1, Figure S5). In the
362 interest of identifying the N₂O hot moments that are most important to measure and mitigate, we
363 recommend whole year analyses as opposed to seasonally subdivided analyses.

364

365 *Evaluation of hot moment threshold determination methods*

366 Our analysis suggests that the 4 SD method was too stringent for hot moment
367 identification, missing what would reasonably be considered hot moments in visual evaluations
368 of the 16 autochamber datasets (Figure S7). By definition, this method should only identify the
369 top 0.1% of the net N₂O flux data as hot moments in datasets exhibiting normal distributions.
370 When we applied the 4 SD method to untransformed right-skewed datasets, approximately 1% of
371 the net N₂O flux data were identified as hot moments (Table 3). On average across the 16
372 autochamber datasets, the 4 SD method yielded ten times higher hot moment threshold values
373 which led to three times lower estimates of hot moment contributions to annual N₂O emissions
374 compared to the 1.5x IQR and IF methods (Table 1, Figure 1). The high threshold values
375 estimated by the 4 SD method not only caused smaller hot moments to be missed but also caused
376 net N₂O fluxes on the rising and falling limbs of large hot moment pulses to be missed (Figure
377 S7). An exception to this stark difference between methods was the autochamber datasets that
378 included extremely high N₂O fluxes following fertilization, which led to comparably high early
379 growing season hot moment contributions (99-100%) estimated by all three methods (Figure 1,
380 Table 2). Our analysis suggests that the 4 SD method would not capture the importance of the
381 smaller-magnitude hot moments to cumulative annual N₂O budgets. We conclude that the 4 SD
382 method is appropriate for identifying the hottest hot moments that are most important to measure
383 and mitigate (Anthony and Silver 2021), but it is likely not ideal for developing comprehensive
384 models of annual N₂O flux patterns because it only effectively hones in on the greatest hot
385 moment triggers.

386 The 1.5x IQR and IF methods yielded similar estimates of hot moment contributions to
387 annual or seasonal N₂O emissions (Figure 1, Figure S5), but the IF method often attributed
388 considerably more net N₂O flux data to hot moments (Figure S6, Table 3). This was due to lower

389 hot moment threshold values estimated by the IF method which led to more N₂O flux data points
390 attributed to hot moments (Table 1, Figure S3). However, these smaller “N₂O hot moments”
391 contributed little to cumulative N₂O emissions over the year or the individual season (Figure S3,
392 Figure S4, Figure 1). This was most exaggerated in the late growing season, which was marked
393 by few and small hot moments across most autochambers. On average across the 16
394 autochamber datasets, the late growing season threshold value estimated by the IF method was
395 so low (ten times lower than that estimated by the 1.5x IQR method), that 89% of late growing
396 season net N₂O flux data points were attributed to hot moments (Figure S4, Table 2). Even in the
397 early growing season when large hot moments occurred, the IF method on average attributed
398 65% of net N₂O flux data points to hot moments (Table 2). The IF method, therefore, appears too
399 permissive in identifying N₂O hot moments which should represent short periods of high net
400 N₂O fluxes that disproportionately contribute to cumulative N₂O emissions (Wagner-Riddle et al.
401 2020). In contrast, the percentage of net N₂O fluxes attributed to hot moments by the 1.5x IQR
402 method was constrained to ~9%, which is more in line with the definition of hot moments (Table
403 3, Figure S6; Wagner-Riddle et al. 2020). We conclude that, of the three threshold determination
404 methods we evaluated, the 1.5x IQR method strikes the best balance in identifying hot moments.
405 Moreover, although there are not yet many published studies that have analyzed high temporal
406 resolution N₂O flux measurements for hot moments, a substantial fraction of published studies
407 have opted to use the 1.5x IQR method (e.g., van den Heuvel et al. 2009, Molodovskaya et al.
408 2012, Li et al. 2015, Bastos et al. 2021), likely because it can robustly detect hot moments even
409 when they vary in flux magnitude.

410

411 *Evaluation of whole year versus seasonally subdivided analyses*

412 Because different mechanisms trigger different magnitude N₂O hot moments in the
413 different seasons, we evaluated seasonally subdivided N₂O flux datasets to ensure that hot
414 moments were appropriately identified in all seasons. While most of the 16 autochamber datasets
415 exhibited large N₂O hot moments in the early growing season and smaller N₂O hot moments in
416 the late- and non-growing seasons (Figure 1, Figure S7), the threshold values estimated from the
417 analysis of whole year datasets did not exclude the smaller N₂O hot moments (Table 1). As such,
418 seasonally subdividing the datasets was not necessary to improve hot moment identification. On
419 the contrary, it detrimentally affected hot moment identification in the early growing season by
420 raising the hot moment threshold value estimated by the 4 SD and 1.5x IQR methods (Table 1).
421 This resulted in a decrease in estimated hot moment contributions to annual N₂O emissions
422 (Figure 1, Table 2). For the IF method, the low threshold values estimated for the late and non-
423 growing seasons led to more than half of those seasons being inappropriately identified as hot
424 moments, thereby increasing the estimated hot moment contribution to annual N₂O emissions
425 relative to whole year analysis (Figure 1). We conclude that seasonal subdivision of N₂O flux
426 datasets can be counterproductive to N₂O hot moment identification and quantification
427 regardless of the threshold determination method.

428

429 **Data Availability Statement**

430 We have uploaded all finalized data to www.scholar.colorado.edu Accession number
431 forthcoming.

432 *Prepublication note: These data are embargoed, pending publication of this manuscript.*

433

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441 disclose.

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