A geostatistical approach to identify and mitigate agricultural nitrous oxide emission hotspots

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Abstract

Anthropogenic emissions of nitrous oxide (N₂O), a trace gas with severe environmental costs, are greatest from agricultural soils amended with nitrogen (N) fertilizer. However, accurate N₂O emission estimates at fine spatial scales are made difficult by their high variability, which represents a critical challenge for the management of N₂O emissions. Here, static chamber measurements ($n = 60$) and soil samples ($n = 129$) were collected at approximately weekly intervals ($n = 6$) for 42-d immediately following the application of N in a southern Minnesota cornfield (15.6-ha), typical of the systems prevalent throughout the U.S. Corn Belt. These data were integrated into a geostatistical model that resolved N₂O emissions at a high spatial resolution (1-m). Field-scale N₂O emissions exhibited a high degree of spatial variability, and were partitioned into three classes of emission strength: hotspots, intermediate, and coldspots. Rates of emission from hotspots were 2-fold greater than

29 non-hotspot locations. Consequently, 36% of the field-scale emissions could be
30 attributed to hotspots, despite representing only 21% of the total field area. Variations in
31 elevation caused hotspots to develop in predictable locations, which were prone to
32 nutrient and moisture accumulation caused by terrain focusing. Because these features
33 are relatively static, our data and analyses indicate that targeted management of hotspots
34 could efficiently reduce field-scale emissions by as much 17%, a significant benefit
35 considering the deleterious effects of atmospheric N₂O.

36 Keywords

37
38 Nitrous oxide; greenhouse gas management; biogeochemical hotspots; LiDAR
39 digital elevation model; geospatial cokriging

40 Abbreviations

41
42 Coefficient of variation, CV; digital elevation model, DEM; light detection and
43 ranging, LiDAR; ordinary cokriging, OC; variable rate nitrogen application, VNRA;
44 wetland probability index, WPI

45 1. Introduction

46
47 Nitrous oxide (N₂O) is a potent greenhouse gas (Hartmann et al., 2013) and the
48 leading cause of stratospheric ozone loss (Ravishankara et al., 2009). In response to its
49 deleterious environmental effects, efforts to mitigate agricultural emissions, which
50 account for nearly 75% of the national anthropogenic source (US Department of State,
51 2014), are in development. Such efforts often focus on N management improvements
52 (e.g., optimizing the source, depth, and timing of fertilizer) at the field or farm scale.

53 Yet, the findings from these mitigation strategies have been highly variable (Venterea et
54 al., 2016), in part because episodic and spatially variable emissions hinder accurate
55 budget estimates (Mathieu et al., 2006; Velthof et al., 2000). For instance, field-scale
56 N₂O emission measurements with chambers can yield a coefficient of variation (CV) as
57 high as 500% (Folorunso and Rolston, 1984; van den Pol-van Dasselaar et al., 1998),
58 suggesting that our ability to accurately determine the outcome of mitigation practices is
59 cause for concern. At fine sub-field spatial scales (<1 m² to 1000 m²), N₂O “hotspots”
60 appear to be disproportionately strong sources (Parkin, 1987; van den Heuvel et al.,
61 2009), yet their influence over cumulative field-scale emissions remains uncertain
62 because high-resolution data are rarely available. For farmers to manage N₂O emissions
63 effectively, subfield-scale emission estimates are necessary to identify potential hotspots
64 and to benchmark their effects on field-scale mitigation practices.

65 Light detection and ranging (LiDAR) digital elevation models (DEMs) are
66 powerful tools that can help guide precision agriculture and conservation strategies
67 (Galzki et al., 2011; Wan et al., 2014). When coupled with geospatial techniques, this
68 emerging technology helps generate high-resolution maps of agriculturally relevant
69 information such as the presence of hydric soils (Fink and Drohan, 2016), moisture
70 content (Moore et al., 1993; Murphy et al., 2009), and soil nitrogen status (Weintraub et
71 al., 2014) that allow farmers to focus extra attention and resources on critical areas.
72 Furthermore, complex processes like methane emissions (Sundqvist et al., 2015) have
73 been characterized using DEMs, suggesting that this technology can better resolve the
74 field-scale spatial distribution of N₂O emissions.

75 Indeed, differences in topography and landscape position have a strong influence
76 on N₂O emissions (Ambus, 1998; Ball et al., 1997) because terrain gradients redistribute
77 moisture and nutrients that are necessary for the production of N₂O. Consequently, N₂O
78 emission frequency distributions are typically positively skewed by a few strong sources
79 (Parkin, 1987; Velthof et al., 2000) observed at topographically low positions (Ambus,
80 1998). Here, terrain focusing enables the development of hotspots by concentrating
81 organic matter, moisture, and nitrate (NO₃⁻) into localized, but potentially predictable
82 areas. Taken together, these soil characteristics can support disproportionately high rates
83 of denitrification (Groffman et al., 2009) that we posit are capable of sustaining high N₂O
84 emissions. However, field-scale emission distribution maps remain coarse, since an
85 unrealistic number of static chambers are required to resolve the high variability,
86 implying poor constraints on hotspots.

87 With the aid of DEMs and geospatial analyses, denitrification hotspots can be
88 isolated and mapped by pinpointing locations with the highest probability of moisture and
89 NO₃⁻ accumulation (Anderson et al., 2015). We propose that a similar approach can
90 resolve the distribution of N₂O emissions at a high spatial resolution that will guide
91 targeted mitigation practices. Here, we examine the spatial distribution of N₂O fluxes
92 and cumulative emissions in a strip-tilled cornfield to address three questions: 1) can
93 DEMs help predict where N₂O hotspots will develop on the landscape; 2) how significant
94 are hotspots in the cumulative field-scale budget; and 3) how can DEMs be used to guide
95 N management and N₂O mitigation?

96 2. Materials and Methods

97 2.1 Site Description and Experimental Design

98

99 The tile-drained, corn-soybean rotation research field (15.6-ha) was located on a
100 private farm 11-km south of Northfield, Minnesota (44°21'37.2"N, 93°12'14.8"W). The
101 predominant underlying soil is a Prinsburg silty clay loam (Typic Endoaquolls, USDA
102 Classification) overlying a loam. Measurements were made during the corn (*Zea mays*,
103 L.) phase in 2014 on DOY 126, 134, 150, 156, 161, and 168. The field was strip-tilled
104 prior to planting and fertilized with 32% urea ammonium sulfate (UAS) on DOY 125 at a
105 rate of 140 kg N ha⁻¹.

106 A 3-m micrometeorological tower was installed on the west side of the field to
107 measure air temperature (VP-4; Decagon Devices, Pullman, WA, USA). Observations
108 were recorded with a data logger at 5-min intervals and averaged hourly (Model EM50;
109 Decagon Devices, Pullman, WA, USA).

110 All soil and chamber sample locations were georeferenced using a GPS device
111 (GeoXH; Trimble, Sunnyvale, CA, USA) connected to a Mi-Fi mobile hotspot (model
112 2200; Verizon Wireless, Wallingford, CT, USA) that boosted the horizontal accuracy to
113 0.1 m. Spatial data were analyzed using ArcMap (ArcGIS v.10.2; ESRI Inc., Redlands,
114 CA, USA).

115 To capture the effects of terrain on N₂O emissions and to ensure potential
116 hotspots were included in the measurement campaign, a Wetland Probability Index (WPI)
117 map was created (ArcGIS v.10.2; ESRI Inc., Redlands, CA, USA) to guide the
118 experimental design. The WPI is a regression function of four factors: the presence of

119 hydric soils, slope, profile curvature, and a compound topographic index (CTI) that is a
120 function of flow accumulation and slope. The WPI provides a relative metric to describe
121 the likelihood that water will pond at a specific location and has been used to identify
122 areas for efficient wetland reclamation (Wan et al., 2014). The WPI was chosen rather
123 than the widely used soil wetness index (SWI), because the WPI incorporates drainage
124 (hydric soils), a recognized shortcoming of the idealized SWI (Murphy et al., 2009). In
125 the context of N₂O production, field locations with wetland terrain characteristics are
126 likely to accumulate moisture and nutrients and are thus candidates for hotspot formation.
127 These areas are likely to experience more frequent and prolonged periods of soil
128 saturation than upland areas, in part because of low slopes and elevation. Using high-
129 resolution (1-m) DEM data (Minnesota Geospatial Information Office) and soil survey
130 information, each position on the landscape was assigned a relative WPI value of 0 to 1
131 (Wan et al., 2014).

132 Since the natural movement of soil moisture is not confined to the explicit 1-m
133 WPI grid, the highest spatial resolution is not necessarily appropriate for direct
134 comparison with a dependent variable (Sørensen and Seibert, 2007). For instance,
135 contour cropping, crop residues, buffer strips and microtopography can affect the
136 movement of moisture. To minimize these uncertainties, we have reduced the WPI
137 resolution to 10-m (Anderson et al., 2015; Zhang and Montgomery, 1994) for direct
138 comparison of N₂O emission measurements and surface characteristics. All other
139 analyses used the high-resolution WPI data set.

140 Because terrain differences can influence emissions, a stratified sampling design
141 based on WPI was used to characterize emission heterogeneity. Groups ($n = 6$) of
142 chambers ($n = 10$) were installed in the field across a range of WPI values on each of the
143 sample dates. Measurements were taken at approximately weekly intervals for 42-d
144 immediately after fertilization (DOY 125). Previous experiments in this field indicate
145 that N_2O fluxes are highest in the 20 to 50-d following fertilization (Baker et al., 2014;
146 Fassbinder et al., 2013). Beyond this time frame, N_2O fluxes decline (Baker et al., 2014;
147 Turner et al., 2016a) and as a result, the cumulative emission budget is most sensitive to
148 loss during this brief period.

149 2.2 Nitrous Oxide Measurements

150
151 Soil N_2O fluxes were measured manually with non-flow-through non-steady-state
152 chambers with a design that has been used extensively in agricultural systems (Maharjan
153 and Venterea, 2014; Maharjan et al., 2014; Venterea and Coulter, 2015). Briefly, each
154 chamber consisted of a stainless steel base inserted 0.05-m into the soil and a removable
155 top (0.50 m x 0.29 m x 0.086 m). Weather stripping and spring clamps attached to
156 opposing sides sealed the chamber headspace from ambient mixing. Each chamber top
157 was vented and covered with an insulated, reflective material. Measurements were taken
158 after at least 48-hr following chamber installation to avoid the potential influence of soil
159 disturbance on the flux.

160 Gas samples were taken from between 0900 and 1500 local time at 0, 15, 30, and
161 45 minute intervals using a 12-mL polypropylene syringe inserted through a butyl rubber
162 septum on the chamber lid. An ambient air sample was taken immediately after chamber

closure. Samples were immediately transferred into glass vials sealed with butyl rubber septa and analyzed within one week using a headspace autosampler (Teledyne Tekmar; Mason, OH, USA) connected to a gas chromatograph (model 5990; Agilent/Hewlett-Packard, Santa Clara, CA, USA) equipped with an electron capture detector. Helium was used as the carrier gas in the GC analyses and the system was calibrated with analytical standards (Scott Specialty Gases, MI) (Bavin et al., 2009). Concentrations from the GC were converted into mass per volume units, assuming ideal gas relations and a known air temperature while sampling.

The slope of the chamber headspace gas concentration was determined using either a linear regression or a quadratic model depending on the curvilinearity of the slope (Parkin et al., 2012; Venterea, 2013). The linear slope was calculated using the SLOPE function (Excel v.2013; Microsoft, Redmond, WA) and the quadratic slope was estimated using the LINEST function at time zero. The quadratic model accounts for suppression of the concentration gradient in response to chamber closure, but is not always necessary. A linear slope was chosen if the second derivative of the quadratic equation was greater than zero (Maharjan et al., 2014). Soil fluxes were calculated using:

$$F = \frac{S \cdot V}{A} \quad \text{Equation 1}$$

where: S is the slope, V is the chamber volume (0.02-m^3), and A (0.14-m^2) is the chamber footprint. Cumulative N_2O emissions were calculated using trapezoidal integration that assumes linearity between sampling periods.

2.3 Soil Analyses

185 Within 24-hours of gas sampling, soil samples ($n = 129$) to a depth of 0.15-m
186 were taken from a georeferenced 35-m grid using a hand corer. Soil samples were
187 weighed within two hours. After drying at 105° C, gravimetric water content (θ) was
188 determined. Using a 2 M KCl extraction, soil NO_3^- concentration was also determined
189 (Maharjan and Venterea, 2014). Extracts were filtered (Whatman no. 1) and NO_3^- was
190 quantified using a flow-through injection analyzer (Lachat, Loveland, CO, USA). The
191 NO_3^- intensity ($\text{NO}_3^-_{\text{int}}$) was calculated using trapezoidal integration (Maharjan and
192 Venterea, 2014; Venterea et al., 2011), which assumes a linear slope between sample
193 dates. Conceptually, $\text{NO}_3^-_{\text{int}}$ represents the cumulative exposure of soil microbes to NO_3^- .
194 The θ intensity (θ_{int}) was calculated similarly. Stepwise regression models were used to
195 identify any terrain indices that were significantly correlated with soil chemical variables.

196 2.4 Geostatistical Analyses

197
198 Interpolations of high-resolution N_2O flux and cumulative emission data were
199 performed with ordinary cokriging (OC) in ArcMap (ArcGIS v.10.2; ESRI Inc.,
200 Redlands, CA, USA). Ordinary cokriging is a geostatistical approach that uses more
201 frequently sampled secondary variables to improve prediction of the primary variable
202 (Vauclin et al., 1983). This method is useful when the primary attribute is costly or
203 logistically more difficult to sample than other correlated variables.

204 Mean N_2O fluxes and cumulative emissions were interpolated at a resolution of 1-
205 m with OC using an omnidirectional “stable” model. Soil NO_3^- and θ were used as
206 secondary variables in this OC model. The sill (variance), nugget (estimate of
207 independent or micro-scale errors), and range (maximum distance of autocorrelation) of

each model were estimated from the semivariogram. The model parameters were optimized for estimation of the range value and neighborhood weights were based on distance. Cross validation was accomplished iteratively by comparing the observation to the OC model predicted value. All inputs were log transformed prior to OC to meet the assumption of normality.

A Getis-Ord G_i^* statistical test identified spatial clustering of high (hotspots) and low (coldspots) emissions at a 95% significance threshold (Ord and Getis, 2010). The field was partitioned into three emission classes based on their respective z -score significance using ArcMap (ArcGIS v.10.2; ESRI Inc., Redlands, CA, USA). Locations with statistically significant high and low z -scores are referred to as emission hotspots and coldspots, respectively. All other values, i.e. those with insignificant ($p > 0.05$) z -scores, are considered “intermediate” locations. A Kruskal-Wallis significance test ($\alpha = 0.05$) was used to determine if there was a WPI difference among emission classes.

3. Results and Discussion

3.1 Meteorology and Soil Characteristics

Over the course of our measurement campaign, this field received 116.8 mm of precipitation and experienced a mean air temperature of 16.4°C. Across all sampling dates, the mean (range) soil NO_3^- concentration and θ content were 20.5 (0-107) $\text{mg NO}_3^- \text{ kg}^{-1}$ and 25% (12-50), respectively (Figure 1). Reported NO_3^- concentration and θ content frequency distributions were positively skewed on each sample date (data not shown), indicating the potential for nutrient processing hotspots. Following fertilization on DOY 125, the daily mean soil NO_3^- concentrations increased until DOY 157, after

231 which they started declining, likely as a result of a combination of leaching,
232 denitrification, and crop uptake.

233 Analyses indicated that the WPI (10-m) was significantly ($p < 0.05$) correlated
234 with θ_{int} and $\text{NO}_3^-_{\text{int}}$ observations ($r^2 = 0.6$ and $r^2 = 0.14$, respectively) (Figure 2). These
235 relationships provide evidence of terrain focusing, implicit in the WPI calculation (e.g.,
236 elevation, slope). Indeed, measurements of θ_{int} were significantly ($p < 0.05$) and
237 negatively correlated with both elevation ($r^2 = 0.6$) and slope ($r^2 = 0.4$). Observations of
238 $\text{NO}_3^-_{\text{int}}$ were not as tightly coupled to elevation ($r^2 = 0.09$) or slope ($r^2 = 0.05$) as θ_{int} ,
239 probably because of the complex N cycling dynamics (i.e. including both production and
240 consumption of NO_3^-) present in soils. Overall, the samples with the highest θ_{int} and
241 $\text{NO}_3^-_{\text{int}}$ were observed in locations with the lowest slope and elevation (Figure 2),
242 suggesting that the soil factors necessary to sustain high denitrification fluxes can become
243 concentrated in predictable areas. This finding provides further support that remote
244 sensing techniques can offer important insights into field-scale N processing dynamics by
245 identifying locations that have an elevated likelihood of moisture and nutrient
246 accumulation (Anderson et al., 2015; Weintraub et al., 2014).

247 3.2 N₂O Emissions

248 3.2.1 Temporal Dynamics

249
250 Across all chambers and sampling dates, the mean (range) N₂O flux was 1.7 (-1 –
251 32) mg N₂O-N m⁻² d⁻¹. The magnitude of N₂O fluxes ranged from 0.7 mg N₂O-N m⁻² d⁻¹
252 on DOY 126, within 24-hrs of fertilization, to a peak emission of 4.3 mg N₂O-N m⁻² d⁻¹
253 on DOY 157, and decreased to a value of 1.8 mg N₂O-N m⁻² d⁻¹ on DOY 168 (Figure 1).

254 Over the sample period, the average N₂O flux was positively correlated ($r^2 = 0.06$; $p <$
255 0.05) to WPI (10-m), indicative of a terrain signal. Indeed, elevation ($r^2 = 0.12$; $p < 0.01$)
256 and slope ($r^2 = 0.04$; $p = 0.06$) correlated with average N₂O fluxes (Figure 3)

257 These hourly mean flux density observations are comparable in strength to a
258 previous study that used 6 automated chambers to estimate the annual N₂O budget at this
259 field site during the 2010 corn phase (Fassbinder et al., 2013). Those investigators
260 determined that N₂O emissions were elevated for 20 to 50 days after fertilization, but
261 then losses declined precipitously and the average hourly standard deviation fell 14-fold,
262 suggesting relatively low temporal measurement uncertainty beyond this brief period
263 (Fassbinder et al., 2013).

264 265 3.2.2 Spatial Dynamics 266

267 Trapezoidal integration of chamber data indicated that the mean (SD) cumulative
268 N₂O emission was 69 (61) mg N₂O-N m⁻² during the 42-d sampling period. We
269 calculated a field-scale CV of 88% from the cumulative chamber data, which is lower
270 than some investigations (Ambus and Christensen, 1995; Ball et al., 1997; Folorunso and
271 Rolston, 1984; Jones et al., 2011; Molodovskaya et al., 2011) and significantly higher
272 than others (Christensen et al., 1996). The reason for our comparatively low CV may
273 have been because our sample size ($n = 60$) was relatively large compared to those
274 previous studies and better captured the spatial heterogeneity. Contrary to our
275 hypothesis, there was not a significant relationship ($r^2 = 0.03$; $p = 0.1$), between the WPI
276 (10-m) and cumulative N₂O emissions (Figure 3). The low r^2 was probably the result of
277 other factors that influence emissions but were not explicitly included in our model, e.g.,

278 pH, gas diffusivity, and sources of N₂O other than denitrification including nitrification
279 (Kool et al., 2011; Venterea et al., 2015). Similarly, slope ($r^2 = 0.04$; $p = 0.08$) was not a
280 significant correlate with N₂O emissions either (Figure 3). However, elevation ($r^2 = 0.09$;
281 $p < 0.05$) exhibited a negative, although weak relation to N₂O emissions (Figure 3),
282 indicating that topographic position can affect N₂O production.

283 Based on *a priori* hypotheses, θ_{int} and $\text{NO}_3^-_{\text{int}}$ were included as secondary OC
284 variables to improve the average N₂O flux and cumulative emission model prediction (n
285 $= 156,190$). Cross-validation of cumulative emissions determined that an
286 omnidirectional stable model was appropriate. Stable model semivariograms indicate
287 that the sill, nugget, and range of the average N₂O flux were 0.59 mg N₂O-N m⁻² d⁻², 0.37
288 mg N₂O-N m⁻² d⁻², and 244-m, respectively, while the sill, nugget, and range of the
289 cumulative emissions were 0.7 mg N₂O-N² m⁻², 0.43 mg N₂O-N² m⁻², and 320-m,
290 respectively (data not shown). As a measure of variance, the sill provides a field-scale
291 estimate of spatial uncertainty, while the nugget is an estimate of either measurement
292 uncertainty or microscale variation (Yanai et al., 2003). Here, a large nugget effect
293 suggests large uncertainty at fine-scales. Observations taken from points separated by a
294 distance greater than the range are no longer spatially autocorrelated, a point identified in
295 the semivariogram where variance becomes asymptotic (i.e. the sill).

296 During the measurement period, the field emitted on average (SD) 1.4 (0.6) mg
297 N₂O-N m⁻² d⁻¹, with a 43% CV, more than half that of the original chamber data (Figure
298 4). Cumulatively, the OC model predicted that 8.7 kg N₂O-N were emitted over the 42-d
299 measurement (Figure 3). This translates to a field-scale mean (SD) cumulative flux of

300 55.4 (22) mg N₂O-N m⁻². The emission distribution was positively skewed, indicating
301 that the data set was likely affected by hotspots. Because soil samples were not taken at
302 each individual chamber, OC interpolations of NO₃⁻_{int} and θ_{int} at each chamber were
303 extracted to assess their relationships with cumulative N₂O emissions. These data show
304 that cumulative N₂O emissions were significantly ($p < 0.01$) correlated with NO₃⁻_{int} ($r^2 =$
305 0.25) and θ_{int} ($r^2 = 0.18$) predictions (Figure 5).

306 Using a Getis Ord Gi* statistical analysis, locations in this field were partitioned
307 into three classes based on their emission strength within the context of neighboring
308 values (Ord and Getis, 2010). These analyses identified significant clustering of high and
309 low N₂O emissions, characteristic of hotspots and coldspots, respectively (Figure 6). The
310 mean (SD) flux from hotspots, intermediate, and coldspot locations was 2.5 (0.4) mg
311 N₂O-N m⁻² d⁻¹, 1.3 (0.3) mg N₂O-N m⁻² d⁻¹, and 0.8 (0.05) mg N₂O-N m⁻² d⁻¹,
312 respectively. Cumulatively, 3.1 kg N₂O-N, 4.6 kg N₂O-N, and 0.9 kg N₂O-N were
313 emitted from hotspots, intermediate, and coldspot locations, respectively.

314 These analyses indicate that a disproportionate share of the field-scale emission
315 budget can be attributed to hotspot locations. Here, hotspots were responsible for 36% of
316 the cumulative N₂O emission budget despite occupying only 21% of the field, while
317 coldspots emitted 11% of the cumulative budget from a comparable area (18%). The
318 remaining N₂O emissions (53%) were lost from intermediate locations, largely because
319 61% of the land surface fell under this emission class. However, the area of a field that
320 qualifies as a hotspot could fluctuate based on meteorology – for instance, a particularly
321 wet spring could increase the surface area of locations that experience prolonged and

322 high moisture exposure. Kruskal-Wallis tests showed that the WPI observed in hotspot
323 locations was greater than the WPI values typically found in the other emission classes,
324 in part because these locations had low slopes and elevation. A Kruskal-Wallis test
325 revealed that hotspots had statistically different slopes (mean = 1.6%) and elevation
326 (mean = 327.8-m) than intermediate (mean = 3.3%; 331.4-m) or coldspot (mean = 3.7%;
327 331.1-m) locations (data not shown).

328 Consequently, the general locations of hotspots were largely static, likely because
329 of the strong relation with topographic indices, including elevation and slope. The
330 positive relations identified here indicate that topography, *via* its controls on nutrient and
331 moisture distributions, can help guide N₂O management practices. Towards this end, the
332 disproportionate strength and stability of N₂O hotspots indicates that targeted
333 management of these sources could efficiently reduce total emissions. For instance, if the
334 average hotspot flux density were reduced from 2.5 mg N₂O-N m⁻² d⁻¹ to 1.3 (0.3) mg
335 N₂O-N m⁻² d⁻¹, a magnitude that is more in step with intermediate areas, the mean field-
336 scale flux density over the entire measurement period could be reduced by up to 14%
337 (10-18). By reducing the cumulative hotspot emissions to 49 (10.4) mg N₂O-N m⁻², the
338 rate observed in intermediate areas, the field-scale budget could be reduced by as much
339 as 17% (12-22). The removal of hotspots through native wetland reclamation could
340 reduce emissions by as much as 36%. Given the strong radiative forcing and other side
341 effects of N₂O, these findings deserve serious consideration, especially if the distribution
342 of potential hotspots is similarly predictable throughout the U.S. Corn Belt.

343 From a management perspective, emission hotspots were generally collocated
344 with NO_3^- hotspots. Consequently, variable rate nitrogen application (VRNA), a recent
345 advancement in precision agriculture, could prove an effective tool to address N_2O
346 hotspots. This technology translates crop reflectance readings into fine-scale fertilizer
347 decisions and has been shown to increase yield and income while providing promising N
348 uptake results (Scharf et al., 2011). Better soil N management overall will potentially
349 reduce N_2O emissions; however, the one-size-fits-all approach to fertilizer application
350 may be a contributing factor to hotspots that VRNA can overcome. For instance, because
351 low-lying areas accumulate surplus NO_3^- from upland areas and may not require
352 additional N, VRNA can limit over application. Further, easing the NO_3^- surplus in
353 upland areas using fine-scale fertilizer decisions could help mitigate the effects of terrain
354 focusing. Alternatively, the selective application of enhanced efficiency N fertilizers
355 (EENFs), which show promising N_2O mitigation results (Halvorson et al., 2014), to
356 hotspots *via* VRNA could minimize their strength. However, extrapolating the effect
357 EENFs may have on hotspots here becomes difficult since EENF results are often
358 specific to soil type and climate.

359 These data also showed that N_2O and θ_{int} hotspots were collocated, suggesting
360 that N_2O hotspots are most likely to require subsurface drainage to ensure crop success.
361 If conservation wetlands or VRNA were capable of reducing NO_3^- losses in tile drainage,
362 either by improving N uptake for target and non-target species (i.e., wetland plants) or by
363 reduced subsurface drainage overall, indirect emissions downstream could also be
364 mitigated (Turner et al., 2016b). A reduction of offsite nitrate losses, like those from

leaching and runoff, would be an important benefit because these can be disproportionately strong sources of N₂O, especially in the Corn Belt (Chen et al., 2016; Griffis et al., 2013; Turner et al., 2015). However, little is known about emissions from conservation wetlands or the ultimate N₂O effect from VRNA.

Since our data set only includes six sample dates, these analyses may not include episodic emissions and therefore likely represent a conservative estimate. To resolve this uncertainty, automated soil chambers are an effective means for taking high frequency measurements (Baker et al., 2014; Turner et al., 2016a). However, sampling constraints (e.g., cost, tube length, and on-site power) tether chambers to a central point, limiting their ability to capture the spatial distribution of emissions observed here. Therefore, the potential for terrain artifacts to bias measurements must be considered when selecting chamber placement. For instance, past work in this field explored various N₂O treatment effects using an automated chamber system (Baker et al., 2014; Fassbinder et al., 2013). Although, those experiments were situated in a location that our analyses has classified as an intermediate strength emitter, they highlight the risks of automated chamber clusters in hotspot or coldspot regions.

4. Conclusion

Our data and analyses have shown that LiDAR DEMs and geospatial techniques can be valuable tools to resolve hotspots and model fine-scale N₂O emissions. Here, hotspots were disproportionately strong sources, responsible for more than a third of the cumulative emissions. Because hotspots are reliant on terrain focusing for nutrients and moisture, they are relatively static features. Consequently, their regularity and

388 predictability should facilitate targeted management practices that could reduce field-
389 scale emissions by as much as 17%.

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397

398 Works Cited

- 399
400 Ambus, P., 1998. Nitrous oxide production by denitrification and nitrification in
401 temperate forest, grassland and agricultural soils. *Eur. J. Soil Sci.*
402 Ambus, P., Christensen, S., 1995. Spatial and seasonal nitrous oxide and methane fluxes
403 in danish forest, grassland, and agroecosystems. *Atmos. Pollut. Trace Gases* 24,
404 993–1001.
405 Anderson, T.R., Groffman, P.M., Walter, M.T., 2015. Using a soil topographic index to
406 distribute denitrification fluxes across a northeastern headwater catchment. *J.*
407 *Hydrol.* 522, 123–134. doi:10.1016/j.jhydrol.2014.12.043
408 Baker, J.M., Fassbinder, J., Lamb, J.A., 2014. The impact of corn stover removal on N₂O
409 emission and soil respiration: An investigation with automated chambers. *Bioenergy*
410 *Res.* 7, 503–508. doi:10.1007/s12155-014-9412-1
411 Ball, B.C., Horgan, G.W., Clayton, H., Parker, J.P., 1997. Spatial variability of nitrous

oxide fluxes and controlling soil and topographic properties. *J. Environ. Qual.* 26,
 1399. doi:10.2134/jeq1997.00472425002600050029x

Bavin, T.K., Griffis, T.J., Baker, J.M., Venterea, R.T., 2009. Impact of reduced tillage
 and cover cropping on the greenhouse gas budget of a maize/soybean rotation
 ecosystem. *Agric. Ecosyst. Environ.* 134, 234–242. doi:10.1016/j.agee.2009.07.005

Chen, Z., Griffis, T.J., Millet, D.B., Wood, J.D., Lee, X., Baker, J.M., Xiao, K., Turner,
 P.A., Chen, M., Zobitz, J., Wells, K.C., 2016. Partitioning N₂O Emissions within
 the US Corn Belt using an Inverse Modeling Approach. *Global Biogeochem.*
Cycles. doi:10.1002/2015GB005313

Christensen, S., Ambus, P., Arah, J.R.M., Clayton, H., Galle, B., Griffith, D.W.T.,
 Hargreaves, K.J., Klemetsson, L., 1996. Nitrous oxide emission from an
 agricultural field: Comparison between measurements by flux chamber and
 micrometeorological techniques. *Atmos. Environ.* 30, 4183–4190. doi:10.1016/1352-
 2310(96)00145-8

Fassbinder, J.J., Schultz, N.M., Baker, J.M., Griffis, T.J., 2013. Automated, low-power
 chamber system for measuring nitrous oxide emissions. *J. Environ. Qual.* 42, 606–
 14. doi:10.2134/jeq2012.0283

Fink, C.M., Drohan, P.J., 2016. High Resolution Hydric Soil Mapping using LiDAR
 Digital Terrain Modeling. *Soil Sci. Soc. Am. J.* 80, 355–363.
 doi:10.2136/sssaj2015.07.0270

Folorunso, O.A., Rolston, D.E., 1984. Spatial Variability Of Field-measured
 Denitrification Gas Fluxes. *Soil Sci. Soc. Am. J.* 48, 1214–1219.

doi:10.2136/sssaj1984.03615995004800060002x

Galzki, J.C., Birr, a. S., Mulla, D.J., 2011. Identifying critical agricultural areas with
three-meter LiDAR elevation data for precision conservation. *J. Soil Water Conserv.*
66, 423–430. doi:10.2489/jswc.66.6.423

Griffis, T.J., Lee, X., Baker, J.M., Russelle, M.P., Zhang, X., Venterea, R., Millet, D.B.,
2013. Reconciling the differences between top-down and bottom-up estimates of
nitrous oxide emissions for the U.S. Corn Belt. *Global Biogeochem. Cycles* 27,
746–754. doi:10.1002/gbc.20066

Groffman, P.M., Butterbach-Bahl, K., Fulweiler, R.W., Gold, A.J., Morse, J.L., Stander,
E.K., Tague, C., Tonitto, C., Vidon, P., 2009. Challenges to incorporating spatially
and temporally explicit phenomena (hotspots and hot moments) in denitrification
models. *Biogeochemistry* 93, 49–77. doi:10.1007/s10533-008-9277-5

Halvorson, A.D., Snyder, C.S., Blaylock, A.D., Del Grosso, S.J., 2014. Enhanced-
efficiency nitrogen fertilizers: potential role in nitrous oxide emission mitigation.
Agron. J. 106, 715. doi:10.2134/agronj2013.0081

Hartmann, D.L., Klein Tank, A.M.G., Rusticucci, M., Alexander, L. V, Brönnimann, S.,
Charabi, Y.A.-R., Dentener, F.J., Dlugokencky, E.J., Easterling, D.R., Kaplan, A.,
Soden, B.J., Thorne, P.W., Wild, M., Zhai, P., 2013. Observations: Atmosphere and
surface, *Climate Change 2013: The Physical Science Basis. Contribution of*
Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on
Climate Change. Cambridge University Press.
doi:10.1017/CBO9781107415324.008

456 Jones, S.K., Famulari, D., Di Marco, C.F., Nemitz, E., Skiba, U.M., Rees, R.M., Sutton,
 457 M. a., 2011. Nitrous oxide emissions from managed grassland: A comparison of
 458 eddy covariance and static chamber measurements. *Atmos. Meas. Tech.* 4, 2179–
 459 2194. doi:10.5194/amt-4-2179-2011

460 Kool, D.M., Dol, J., Wrage, N., Willem, J., Groenigen, V., 2011. Soil Biology &
 461 Biochemistry Nitrifier denitrification as a distinct and significant source of nitrous
 462 oxide from soil. *Soil Biol. Biochem.* 43, 174–178. doi:10.1016/j.soilbio.2010.09.030

463 Maharjan, B., Venterea, R.T., 2014. Anhydrous ammonia injection depth does not affect
 464 nitrous oxide emissions in a silt loam over two growing seasons. *J. Environ. Qual.*
 465 43, 1527–1535. doi:10.2134/jeq2014.07.0292

466 Maharjan, B., Venterea, R.T., Rosen, C., 2014. Fertilizer and irrigation management
 467 effects on nitrous oxide emissions and nitrate leaching. *Agron. J.* 106, 703–714.
 468 doi:10.2134/agronj2013.0179

469 Mathieu, O., Lévêque, J., Hénault, C., Milloux, M.J., Bizouard, F., Andreux, F., 2006.
 470 Emissions and spatial variability of N₂O, N₂ and nitrous oxide mole fraction at the
 471 field scale, revealed with ¹⁵N isotopic techniques. *Soil Biol. Biochem.* 38, 941–951.
 472 doi:10.1016/j.soilbio.2005.08.010

473 Molodovskaya, M., Warland, J., Richards, B.K., Öberg, G., Steenhuis, T.S., 2011.
 474 Nitrous oxide from heterogeneous agricultural landscapes: Source contribution
 475 analysis by eddy covariance and chambers. *Soil Sci. Soc. Am. J.* 75, 1829.
 476 doi:10.2136/sssaj2010.0415

477 Moore, I.D., Gessler, P., Nielsen, G.A., Peterson, G.A., 1993. Soil attribute prediction

478 using terrain analysis. *Soil Sci. Soc. Am. J.* 57, 443–452.
 479 doi:10.2136/sssaj1993.572NPb

480 Murphy, P.N.C., Ogilvie, J., Arp, P., 2009. Topographic modelling of soil moisture
 481 conditions: A comparison and verification of two models. *Eur. J. Soil Sci.* 60, 94–
 482 109. doi:10.1111/j.1365-2389.2008.01094.x

483 Ord, J.K., Getis, A., 2010. Local spatial autocorrelation statistics: Distributional issues
 484 and an application. *Geogr. Anal.* 27, 286–306. doi:10.1111/j.1538-
 485 4632.1995.tb00912.x

486 Parkin, T.B., 1987. Soil microsites as a source of denitrification variability. *Soil Sci. Soc.*
 487 *Am. J.* 51, 1194–1199. doi:10.2136/sssaj1987.03615995005100050019x

488 Parkin, T.B., Venterea, R.T., Hargreaves, S.K., 2012. Calculating the detection limits of
 489 chamber-based soil greenhouse gas flux measurements. *J. Environ. Qual.* 41, 705.
 490 doi:10.2134/jeq2011.0394

491 Ravishankara, A.R., Daniel, J.S., Portmann, R.W., 2009. Nitrous oxide (N₂O): The
 492 dominant ozone-depleting substance emitted in the 21st century. *Science* 326, 123–
 493 125. doi:10.1126/science.1176985

494 Scharf, P.C., Shannon, D.K., Palm, H.L., Sudduth, K.A., Drummond, S.T., Kitchen,
 495 N.R., Mueller, L.J., Hubbard, V.C., Oliveira, L.F., 2011. Sensor-based nitrogen
 496 applications out-performed producer-chosen rates for corn in on-farm
 497 demonstrations. *Agron. J.* 103, 1683–1691. doi:10.2134/agronj2011.0164

498 Sørensen, R., Seibert, J., 2007. Effects of DEM resolution on the calculation of
 499 topographical indices: TWI and its components. *J. Hydrol.* 347, 79–89.

doi:10.1016/j.jhydrol.2007.09.001

Sundqvist, E., Persson, A., Kljun, N., Vestin, P., Chasmer, L., Hopkinson, C., Lindroth, A., 2015. Upscaling of methane exchange in a boreal forest using soil chamber measurements and high-resolution LiDAR elevation data. *Agric. For. Meteorol.* 214-215, 393–401. doi:10.1016/j.agrformet.2015.09.003

Turner, P.A., Baker, J.M., Griffis, T.J., Venterea, R.T., 2016a. The impact of kura clover living mulch on nitrous oxide emissions in a corn/soybean system. *J. Environ. Qual.* doi:10.2134/jeq2016.01.0036

Turner, P.A., Griffis, T.J., Baker, J.M., Lee, X., Crawford, J.T., Loken, L.C., Venterea, R.T., 2016b. Regional-scale controls on dissolved nitrous oxide in the Upper Mississippi River. *Geophys. Res. Lett.* 43, 4400–4407. doi:10.1002/2013GL058740

Turner, P.A., Griffis, T.J., Lee, X., Baker, J.M., Venterea, R.T., Wood, J.D., 2015. Indirect nitrous oxide emissions from streams within the US Corn Belt scale with stream order. *Proc. Natl. Acad. Sci.* 112, 9839–9843. doi:10.1073/pnas.1503598112

US Department of State, 2014. 2014 United States Climate Action Report.

van den Heuvel, R.N., Hefting, M.M., Tan, N.C.G., Jetten, M.S.M., Verhoeven, J.T.A., 2009. N₂O emission hotspots at different spatial scales and governing factors for small scale hotspots. *Sci. Total Environ.* 407, 2325–2332. doi:10.1016/j.scitotenv.2008.11.010

van den Pol-van Dasselaar, A., Corré, W.J., Priemé, A., Klemetsson, Å.K., Weslien, P., Klemetsson, L., Stein, A., Oenema, O., 1998. Spatial variability of methane, nitrous oxide, and carbon dioxide emissions from drained grasslands. *Soil Sci. Soc.*

Am. J. 62, 810–817. doi:10.2136/sssaj1998.03615995006200030039x

Vaucelin, M., Vieira, S.R., Vachaud, G., Nielsen, D.R., 1983. The Use of Cokringing with Limited Field Soil Observations. *Soil Sci. Soc. Am. J.* 47, 175–184.

Velthof, G.L., van Groenigen, J.W., Gebauer, G., Pietrzak, S., Jarvis, S.C., Pinto, M., Corré, W., Oenema, O., 2000. Temporal stability of spatial patterns of nitrous oxide fluxes from sloping grassland. *J. Environ. Qual.* 29, 1397. doi:10.2134/jeq2000.00472425002900050005x

Venterea, R.T., 2013. Theoretical comparison of advanced methods for calculating nitrous oxide fluxes using non-steady state chambers. *Soil Sci. Soc. Am. J.* 77, 709. doi:10.2136/sssaj2013.01.0010

Venterea, R.T., Bijesh, M., Dolan, M.S., 2011. Fertilizer source and tillage effects on yield-scaled nitrous oxide emissions in a corn cropping system. *J. Environ. Qual.* 40, 1521–1531. doi:10.2134/jeq2011.0039

Venterea, R.T., Clough, T.J., Coulter, J. a., Breuillin-Sessoms, F., 2015. Ammonium sorption and ammonia inhibition of nitrite-oxidizing bacteria explain contrasting soil N₂O production. *Sci. Rep.* 5, 12153. doi:10.1038/srep12153

Venterea, R.T., Coulter, J.A., 2015. Split application of urea does not decrease and may increase nitrous oxide emissions in rainfed corn. *Agron. J.* 107, 337. doi:10.2134/agronj14.0411

Venterea, R.T., Coulter, J.A., Dolan, M.S., 2016. Evaluation of Intensive “4R” Strategies for Decreasing Nitrous Oxide Emissions and Nitrogen Surplus in Rainfed Corn. *J. Environ. Qual.* doi:10.2134/jeq2016.01.0024

544 Wan, H., Mulla, D.J., Galzki, J.C., 2014. Using LiDAR and geographic information
 545 system data to identify optimal sites in southern Minnesota for constructed wetlands
 546 to intercept nonpoint source nitrogen. *J. Soil Water Conserv.* 69, 115A–120A.
 547 doi:10.2489/jswc.69.4.115A

548 Weintraub, S.R., Taylor, P.G., Porder, S., Cleveland, C.C., Asner, G.P., Townsend, A.R.,
 549 2014. Topographic controls on soil nitrogen availability in a lowland tropical forest.
 550 *Ecology* 96, 1561–1574. doi:10.1890/14-0834.1

551 Yanai, J., Sawamoto, T., Oe, T., Kusa, K., Yamakawa, K., Sakamoto, K., Naganawa, T.,
 552 Inubushi, K., Hatano, R., Kosaki, T., 2003. Atmospheric Pollutants and Trace Gases
 553 Factors in an Agricultural Field. *J. Environ. Qual.* 32, 1965–1977.

554 Zhang, W., Montgomery, D.R., 1994. Digital elevation model grid size, landscape
 555 representation, and hydrologic simulations 30, 1019–1028.

556

Figure 1. Boxplots of a) NO_3^- concentration ($\text{mg NO}_3^- \text{ kg}^{-1}$), b) gravimetric moisture content (%), and c) N_2O flux density ($\text{mg N}_2\text{O-N m}^{-2} \text{ d}^{-1}$). Red points designate outliers.

Figure 2. Plotted relationships between topographic indices and soil characteristics ($n = 129$). Top row). Mean soil NO_3^- concentration (blue dots); mean gravimetric water content (θ ; green triangles). Bottom row). Integrated soil NO_3^- ($\text{NO}_3^-_{\text{int}}$; blue dots); integrated gravimetric water content (θ_{int} ; green triangles).

Figure 3. Plotted relationships between mean N₂O fluxes (a, b, and c) and cumulative N₂O emissions (d, e, and f) over the measurement period against topographic indices ($n = 60$).

Lines of linear best fit (red lines) for each graph are included.

Figure 4. The Wetland Probability Index (WPI) overlain with chamber measurements (blue circles) and soil samples (red diamonds). Results are presented from the N_2O ordinary cokriging model, which interpolated mean flux density and cumulative emissions at a 1-m spatial resolution.

Figure 5. The relationship between cumulative N₂O emissions and the soil characteristics, NO_3^- and θ_{int} . A linear line of best fit is included (red).

Figure 6. Results from the Getis Ord Gi* statistic that was used to identify the spatial distribution of hotspots and coldspots. Intermediate locations are transparent.

Graphical Abstract