Temporal Variability of Nitrous Oxide from Fertilized Croplands: Hot Moment Analysis

Nitrous oxide ($N_2O$) emissions were monitored using the micrometeorological eddy covariance technique from manure-fertilized cropland on a large dairy farm in New York State in 2006 to 2009. Nitrous oxide emissions demonstrated episodic behavior with intermittent short-duration peak fluxes up to 39.7 mg $N_2O$-N m$^{-2}$ d$^{-1}$, whereas most of background fluxes during the annual agricultural cycle were below 6.5 mg $N_2O$-N m$^{-2}$ d$^{-1}$. This paper discusses temporal variability of measured $N_2O$ emissions using a “hot moment” approach. To identify and quantify peak events as potential hot moments and to determine whether or not they could be treated statistically as outliers, $N_2O$ daily fluxes were analyzed by the box plot method using multiple thresholds. Peak events exceeding outlier thresholds contributed up to 51% of cumulative annual $N_2O$ emissions, although they represented <7% of the total observation time. Individual $N_2O$ peaks were also categorized by their duration, as single day spikes and multiday events. The highest contributing instances were multiday $N_2O$ peaks during summer precipitation and early spring thaw, largely enhanced by manure fertilization. These high-intensity emission events demonstrated repetitive seasonal responses to a combination of environmental factors and were therefore identified as hot moments. Abrupt rises in both temperature and soil moisture appeared to trigger major hot moments, whereas the availability of manure N controlled their magnitude. In the absence of strong correlations between time-series of individual environmental factors and $N_2O$ emissions, the hot moment approach can be a promising tool for the integrated analysis of most significant $N_2O$ events in cultivated fields receiving manure applications.

Abbreviations: EC, eddy covariance; WFPS, water-filled pore space.

The potential adverse effects of agriculturally-produced $N_2O$ as a greenhouse gas and stratospheric ozone destructor are a serious concern in environmental science and policy. Manure fertilization of agricultural lands considerably increases $N_2O$ emissions (Bouwman et al., 2002; Kroeze et al., 1999; Mosier et al., 1998). Nitrous oxide generated from manure-amended soils is formed through several microbiological and chemical processes, primarily via autotrophic nitrification of ammonium and heterotrophic denitrification of soil nitrates and nitrites (Anderson et al., 1993; Barnard et al., 2005; Bremner, 1997). Despite ongoing research into emission rates and underlying processes, there is still uncertainty in quantification and prediction of agricultural $N_2O$ emissions (Desjardins et al., 2010; Pfeil et al., 2007), largely due to its high temporal variability.

Measured $N_2O$ emissions from fertilized cropland fall within a wide range: 0.7 to 51.8 mg $N_2O$–N m$^{-2}$ d$^{-1}$ (Drury et al., 2006; Goodroad et al., 1984; Khalil et al., 2002; Laville et al., 1999; Neftel et al., 2007; Rochette et al., 2004; Sehy et al., 2003; Venterea et al., 2005; Wagner-Riddle and Thurtell, 1998). Field studies also
report episodic \(\text{N}_2\text{O}\) behavior, in which short-lasting peak events exceed background emission levels by orders of magnitude and contribute up to a half of the total annual flux. Parkin and Kaspar (2006) showed such events accounted for 45 to 49% of the cumulative annual \(\text{N}_2\text{O}\) flux monitored at fertilized corn fields for two consecutive years. In 3 mo of continuous measurements on a dairy farm on peat land in the Netherlands, 40% of total \(\text{N}_2\text{O}\) emission was due to a single event (Kroon et al., 2007). During an 8-mo eddy covariance \(\text{N}_2\text{O}\) study, Scanlon and Kiely (2003) documented three major emission peaks events which covered a timeframe of 16 d (6.6% of total monitoring time) and contributed 51% of the cumulative flux.

This episodic nature of \(\text{N}_2\text{O}\) fluxes can be described using a hot moment approach. A hot moment in biogeochemistry is defined as a brief and disproportionately high biogeochemical response (e.g., the short-term \(\text{N}_2\text{O}\) flux event) to the combination of multiple influencing factors or “reactants” (McClain et al., 2003). The presence of all reactants is required for the formation of a hot moment; if one or more is missing, a hot moment does not occur. Incorporating hot moments into \(\text{N}_2\text{O}\) flux estimates, and understanding their seasonal distribution and factors of influence, is necessary for improved prediction and modeling of terrestrial \(\text{N}_2\text{O}\) emissions (Groffman et al., 2009). To our knowledge, no previous study has focused on the identification and analysis of \(\text{N}_2\text{O}\) hot moments or environmental factors triggering \(\text{N}_2\text{O}\) hot moments. Although it is well known that seasonal changes in soil moisture, temperature, and \(\text{N}\) availability strongly influence \(\text{N}_2\text{O}\) emissions (Goodroad et al., 1984; Wagner-Riddle et al., 2007), their complex interplay and combined effect on \(\text{N}_2\text{O}\) pulses is still poorly understood.

The lack of information on hot moments is partly due to the challenges in \(\text{N}_2\text{O}\) monitoring. A continuous, long-term, high-frequency and high-precision flux methodology is required to capture short-lived and often sporadic \(\text{N}_2\text{O}\) peak events. Static closed flux chambers are commonly used for \(\text{N}_2\text{O}\) measurements, especially in process-level and spatial distribution studies, but their low sampling frequency (typically a single half-hour period at semi-weekly to semi-monthly intervals) limits their suitability for \(\text{N}_2\text{O}\) temporal variability studies (Molodovskaya et al., 2011; Parkin, 2008; Singurindu et al., 2009; Yates et al., 2006). Eddy covariance (EC), a micrometeorological methodology based on high-frequency (10 Hz) measurements of greenhouse gas concentration and vertical wind speed (Baldocchi, 2003), enables high-resolution flux monitoring that is less labor-intensive and thus more suitable for the long-term studies of \(\text{N}_2\text{O}\) temporal patterns (di Marco et al., 2004; Nefel et al., 2007; Pattey et al., 2006). It however remains relatively uncommon due to the high cost of current instrumentation and demanding data management.

The aim of this study is to analyze temporal and seasonal variability of long-term \(\text{N}_2\text{O}\) emissions monitored by the EC method from dairy manure-fertilized croplands using the hot moment approach. This paper discusses the basic steps for \(\text{N}_2\text{O}\) hot moment quantification, particularly, the choice of numerical thresholds for elevated \(\text{N}_2\text{O}\) flux events, which potentially constitute hot moments. The occurrence of the fluxes above the thresholds and their contribution to the cumulative annual \(\text{N}_2\text{O}\) emission is analyzed. The relationship between \(\text{N}_2\text{O}\) flux peak events and combined environmental factors is investigated. The discussion focuses on identification and formation of potential \(\text{N}_2\text{O}\) hot moments within the annual agricultural cycle observed during a long-term study of manure-fertilized fields monitored from 2006 to 2009 in New York State.

**MATERIALS AND METHODS**

**Research Sites**

Eddy covariance monitoring of \(\text{N}_2\text{O}\) fluxes was conducted on manure-fertilized fields of a large dairy farm located in Harford, NY, (42°25′34″ N, 76°13′36″ W). The area has a humid continental climate with mean annual temperature of 7.8°C, mean annual precipitation of 932 mm, and snowfall of 175 cm (NRCC, 1980–2010). The length of the freeze-free season varies from 120 to 150 d. The soils on the research sites are well-drained, Howard gravelly loam (loamy-skeletal, mixed, active, mesic Glossic Hapludalf) with 120, 450, 430, and 40 g kg⁻¹ for clay, sand, silt, and organic matter, respectively; the slope across the monitored fields was ~1.2% (USDA, 2006).

Nitrous oxide studies were performed at two sites with identical soil and climate conditions. The first site was an alfalfa field (Medicago sativa L.) monitored during the growing season (April–October) of 2006 (field A, area 24.8 ha, Fig. 1). In 2007, the experimental setup was moved to a second site (adjacent fields B and C, area 15.6 and 14.1 ha, Fig. 1), that was planted with corn (Zea mays L.). Monitoring continued at that site in 2008-2009, during which time field B was kept in corn, and field C was rotated to alfalfa. The fields were tilled (moldboard-plowed for corn and chisel-plowed followed by disc harrowing for alfalfa) before planting in early spring.

**Manure Applications**

All fields received semi-solid and/or liquid manure annually in 2006 to 2008; synthetic fertilizers were not applied during the time of experiment. Long-term manure storage was not available, and manure spreading was determined by the farm management needs and field availability and thus not controlled by the research group. Manure loads and periods of application are shown in Table 1. During those periods small loads of manure (3–8 t ha⁻¹ d⁻¹) were applied to the fields daily. No spreading occurred in 2009.

**Eddy Covariance System**

The eddy flux of \(\text{N}_2\text{O}\) was calculated as a product of instantaneous changes in vertical wind velocity and \(\text{N}_2\text{O}\) gas concentration (Pattey et al., 2006), which were measured by 3-D sonic anemometer (model CSAT3; Campbell Scientific, Inc., Logan, UT) and a TGA100A Tunable Diode Laser Absorption Spectrometry/Trace Gas Analyzer (TDLAS/TGA; Campbell Scientific, Inc.), respectively.
The TGA sampling inlet and 3-D anemometer were mounted to a tripod mast at a height of 3.5 m throughout the study, and the distance between anemometer sonic transducers and the TGA sample inlet was 5 cm. The sonic axis of the sonic anemometer was oriented along the local prevailing wind direction (285° WNW; Fig. 1). The TGA100A analyzer was located on the ground at the base of the measurement mast to minimize the length of sample intake tubing (3.2 mm i.d., ~4 m length). The lag time for air travel between sample intake and N₂O detector was determined from field testing to be 0.7 s, and the time series of N₂O concentration and wind speed were accordingly lag-synchronized for EC calculations. Sample air was drawn through the TGA’s N₂O sample cell under 50 to 55 mbar with a rotary vane vacuum pump (model RB0021; Bush, Inc., Virginia Beach, VA) installed ~70 m downwind from the mast/TGA location. Air moisture was removed via purge flow through a diffusive dryer (PD1000, Perma Pure, Inc., Toms River, NJ) installed between the sample intake and the TGA. Air particulates were removed with a disposable 10.0-μm polypropylene filter on the dryer’s inlet (changed biweekly). The total air flow rate was 18 L min⁻¹, and the purge flow rate was 3 L min⁻¹, leaving a flow of 15 L min⁻¹ through the analyzer. The N₂O signal was measured at 2205 cm⁻¹ laser absorption line and 723 mA laser DC current. A certified standard reference N₂O gas with a flow rate of 10 cm³ min⁻¹ simultaneously passed through the reference cell. The reference signal provides a template for the shape of the spectrum and allows the sample concentration to be determined independently from temperature or pressure of the sample gas or the spectral positions of the scan samples. The reference signal also provides feedback for an internal control algorithm that locks the center of the spectral scan at the center of the desired absorption line (TGA 100A Trace Gas Analyzer Overview; Campbell Scientific, Inc.). The reference cell is much shorter than the sample cell, so the high concentration reference gas (2000 ppm N₂O in N₂) was used to provide more comparable detector response. The laser was cooled by liquid nitrogen (LN2, refilled every 6 d) to an operating temperature of 88.6°K. The system was continuously powered by a gasoline generator with a supplemental fuel tank installed downwind from the mast at the first location in 2006 (Fig. 1), and then by line power at the second site. The measurement frequency was 10 Hz (every 0.1 s), with half-hourly fluxes calculated from the high frequency data. All data were collected using a Model CR5000 data logger (Campbell Scientific, Inc.) and stored and transferred with an industrial grade compact flash card.

The detection limit σₓ of the EC measurements was calculated using the formula (Pihlatie et al., 2005):

Table 1. Manure N loads and application schedule at Cornell T&R Center in 2006 to 2008, Harford, NY.

<table>
<thead>
<tr>
<th>Year and site (crop)</th>
<th>Manure application period</th>
<th>Total number of manure spreading days</th>
<th>Daily manure load</th>
<th>Manure N applied</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Total N</td>
</tr>
<tr>
<td>2007, fields B+C (both corn)</td>
<td>22 Dec. 2006–15 Mar. 2007</td>
<td>85</td>
<td>3.2</td>
<td>1296</td>
</tr>
</tbody>
</table>
where \( \sigma_x \) is the noise level of the TDLAS system calculated as the square root from the two-sample variance (nmol mol\(^{-1}\)), \( \sigma_w \) is the standard deviation of vertical wind speed (m s\(^{-1}\)), \( T \) is the averaging period (s), and \( f \) is the measurement frequency. The noise level was estimated as 1.5 nmol mol\(^{-1}\), and the vertical wind speed standard deviation was 0.09 m s\(^{-1}\). For a 30-min averaging period with 10-Hz measurement frequency, the method’s detection limit was 1 ng N\(_2\)O-N m\(^{-2}\) s\(^{-1}\). For daily averaging period, the detection limit was 0.15 ng N\(_2\)O-N m\(^{-2}\) s\(^{-1}\) or 0.013 mg N\(_2\)O-N m\(^{-2}\) d\(^{-1}\).

### Data Quality Control and Analysis

Data quality control was conducted in two steps. The first step was eliminating poor-quality half-hour data averages obtained during technical shutdowns, interruptions, and routine laser maintenance (data corresponding to TGA internal pressures of less than 45 mbar or more than 60 mbar, and TGA laser temperatures >88.6°K). The second step was performed on the half-hour data before the covariance calculations. Covariances were calculated using the natural coordinate system (Tanner and Thurtell, 1969). The data with friction wind velocity ≤0.1 m s\(^{-1}\) and horizontal wind speed ≤1.5 m s\(^{-1}\) were discarded to exclude measurements occurring when turbulent mixing was not sufficient, as recommended by Pattey et al. (2006). To remove potential disturbances to the wind from the warehouse located downwind and the mast itself, data associated with wind directions ≥120° and ≤120° from the pointing direction of the sonic anemometer (azimuth of 45° NE and 165° SSE) were also discarded. The “clean” half-hour flux data were then averaged to the daily means. The minimum threshold for averaging half-hour to daily fluxes was 25% or 12 half-hour data points per day. The data filtering resulted in quality-assured data that represented 51% of raw data collected in 2006, 72% in 2007 and 69% in 2008-2009, which is consistent with the average percentage of eddy flux data recovery of 65% on the FLUXNET sites (Falge et al., 2001). More frequent downtimes due to generator failures and maintenance needs contributed to the lower fraction of quality-assured data in 2006. Flux calculations and quality control analysis were performed using Matlab, version 7.0 (MathWorks, Inc., Natick, MA).

### Soil and Weather Parameters

Air temperature was monitored automatically throughout the study by a HMP45A/D probe (Vaisala Group) mounted on the EC mast at 3.5 m height, next to the sonic anemometer. Soil temperature measurements were added in July 2007 with four thermocouple probes (potted in 2.5cm length of 1 cm diam. copper tubing with heat-conducting epoxy) installed 10 cm below the soil surface.

Soil moisture was monitored manually on a weekly basis at five locations around the mast (HydroSense CS620, 12 cm probe, Campbell Scientific, Inc.) from April to October in 2006. Continuous high-frequency measurements of soil moisture at 10-cm depth from two locations near the mast were added to the instrumentation suite in July 2007 (CS616 Water Content Reflectometers, Campbell Scientific, Inc.). The CS620 and CS616 soil moisture sensors were field-calibrated using the standard soil-core gravimetric method, and the calibration coefficient was determined from a curve fit to measured water content values and sensor output. Precipitation was measured using a tipping bucket rain gauge (model 3665R, Spectrum Technologies). All weather parameters were monitored automatically every 5 min, and then averaged into half-hour and daily data, unless noted otherwise.

Soil samples from the top 10 cm were collected bi-monthly in 2006 and monthly thereafter during the growing season using a 5-cm (i.d.) aluminum step-down soil probe. Each sampling consisted of five cores taken from each treatment at the distances of 2, 5, 10, 20, and 50 cm from the mast. The samples were refrigerated at 4°C before analysis. For gravimetric moisture content and bulk density determination, samples were oven-dried at 105°C for 24 h. The NO\(_2\)/NO\(_3\)–N contents were analyzed after extraction with 2 M KC\(_2\). For extract preparation, 5 g of field-moist soil were placed in centrifuge tubes with 50 mL of 2 M KC\(_2\), shaken for 30 min, centrifuged at 3000 rpm for 40 min, and filtered through 0.45-μm membrane filters ( Pall Life Science Corp., Port Washington, NY). The supernatant was analyzed for NO\(_2\)/NO\(_3\)–N colorimetrically by the sulfanilamide method using a continuous flow spectrophotometer (Astoria Analyzer; Astoria Pacific, Inc., Clackamas, OR).

### Statistical Analysis of Nitrous Oxide Time Series and Peak Events

The N\(_2\)O daily data were tested for normality using the Shapiro–Wilk test (SigmaPlot 11.0; Systat Software, Inc., Chicago, IL). The time series were analyzed for autocorrelation and cross-correlation between N\(_2\)O flux, temperature, precipitation, and soil moisture data in R (R Development Core Team, 2011).

To identify numerical thresholds for N\(_2\)O peak events as potential hot moments, the daily fluxes for each year were analyzed using the box plot method (SigmaPlot 11.0; Systat Software Inc.) commonly used for outlier analysis (Dowdy et al., 2004). The advantage of the box plot (besides its simplicity compared to other outlier tests) is that it links the magnitude of the numerical event to the median and not the mean, and therefore can be used even when the flux data are not normally distributed (Walsh, 2006).

The box plot method is based on calculating the lower quartile Q1 (25th percentile), upper quartile Q3 (75th percentile), and the median (50th percentile). The upper (UF) and lower (LF) fences are set at a fixed distance (\( n \) times) from the interquartile range:

\[
UF = Q3 + n(Q3 – Q1) \tag{2}
\]

\[
LF = Q1 – n(Q3 – Q1) \tag{3}
\]
Any observation outside these fences is an outlier.

In this study, we applied the mild ($n = 1.5$) UF calculated by the box plot method as a major threshold to identify the N$_2$O peak events and potential hot moments. Two additional thresholds, the extreme ($n = 3.0$) UF and the 75th percentile, were also tested as the peak event highest and lowest bounding estimates, respectively. All N$_2$O daily fluxes above those thresholds were analyzed for their timeframe, magnitude, contribution to the annual flux and responsiveness to environmental changes. The three thresholds and resulting hot moments were then evaluated and compared to determine the sensitivity and representativeness of the thresholds, including the proportion of the total annual N$_2$O flux represented by hot moments at each threshold level.

RESULTS
Nitrous Oxide Time Series
Daily N$_2$O fluxes from both sites were generally below 6.5 mg N$_2$O-N m$^{-2}$ d$^{-1}$ (90%), whereas intermittent peaks reached up to 39.7 mg N$_2$O-N m$^{-2}$ d$^{-1}$ (Fig. 2). The variability of N$_2$O fluxes was high for all years, with coefficients of variation between 160 and 236% (Table 2). Approximately 26% of the daily fluxes were below the method detection limit of 0.013 mg N$_2$O-N m$^{-2}$ d$^{-1}$. Out of all fluxes above the detection limit, 73% were positive (indicating soils as a source of N$_2$O to the atmosphere). The normality test showed that daily N$_2$O fluxes were highly skewed and not normally distributed ($P < 0.001$) with the probability distribution being reverse J-shaped (Fig. 3), similar to previous observations (Wagner-Riddle et al., 2007; Yates et al., 2006).

Cross-correlation analysis between the time-series showed little correlation ($r = 0.15$) between N$_2$O flux and air temperature at zero time lag (with smaller $r$ values for lags of 1 d and greater). Correlation between N$_2$O flux and precipitation was strongest ($r = 0.15$) at 8-d time lag, and no significant correlation was found between fluxes and soil moisture (expressed as water-filled pore space).

Nitrous Oxide Peak Events: Timeframe, Magnitude, and Contribution to the Annual Flux
Annual N$_2$O thresholds for potential hot moments are shown in Fig. 4 and Table 3. The magnitude of thresholds generally followed the annual median trend, except for 2008. The difference in threshold values between the years varied within 50% in all threshold categories (Table 3).

Above-threshold daily N$_2$O flux events (from this point called “peak events”) in all categories occurred each year (Table 3). Fewer peak events were documented in 2006 and 2009, as those datasets were from incomplete years of observations (April–October 2006 and January–May 2009). Normalizing the number of peak event days to the total days of observations showed that the peak event timeframe, as percentage of total time, was similar for 2007, 2008, and 2009, only slightly varying within the threshold categories: 20 to 21% in 75th percentile, 5 to 7% in the mild, and 2 to 3% in the extreme category. In contrast, the 2006 peak event timeframe in each category was much shorter, approximately half of those in 2007 to 2009. Among the threshold categories, the difference in peak event timeframe was greater between 75th percentile and the mild categories (factor of 3–4) than between the mild and extreme categories (factor of 2).

The greatest annual values for peak events were documented in early spring (March–April) for 2007 to 2009 and in July for 2006 (Table 2). The smallest events in the 75th percentile category occurred in May–June of each year and varied between 2.8 and 4.8 mg N$_2$O-N m$^{-2}$ d$^{-1}$.

The contribution of N$_2$O peak events, as potential hot moments, to the net cumulative measured emissions (total of positive and negative fluxes) is shown in Table 3. For various years, peak events above the 75th percentile contributed between 71 and 102% of total net emissions. Values >100% of net N$_2$O emissions in 2008 indicate a substantial negative flux detracting from the net amount. The peak event contributions were least variable interannually in the mild outlier category, ranging from 40% of total emissions in 2006 up to 51% in 2008. In the extreme outlier category, the lowest peak event contribution was observed in 2009 (11% of total) as compared to the 2006 to 2008 contributions, which showed only slight variation (27-28%; Table 3).

A percent contribution to the net emissions from a single peak event was also calculated (Table 3). Among categories, the tendency was opposite to the total peak event contributions: an average single N$_2$O peak event in the extreme category contributed up to three times more to the total than an average peak event above 75th percentile. Between years, the greatest single peak event contribution was observed in 2006 for each category, even though the total contributions in 2006 were the smallest in two (75th percentile and mild) of three categories.

Nitrous Oxide Peak Event Temporal Distribution
The temporal distribution of the N$_2$O peak events demonstrated two patterns: spikes and multiday peaks. A spike is defined here as a single-point peak event lasting for no longer than 1 d. Multiday peak is defined as a number of contiguous N$_2$O daily fluxes that formed a prolonged peak lasting for two or more days.

The N$_2$O spikes and multiday peaks are shown for each year in each threshold category in Table 4. It should be noted single data points which appeared as top-of-the-peak values in the higher threshold (mild and extreme) categories but constituted multiday peaks in the lower categories were assigned to the multiday peak group. A total of 78 spikes were documented in the 75th percentile threshold category, five of those also passed the mild outlier threshold, and only one spike passed the extreme outlier threshold. The number of multiday peak events was 38 in 75th percentile category (133 total days), 22 in mild category (52 total days) and 12 in extreme category (25 total days). Spikes and multiday peaks were sometimes observed in combinations, when a single-day peak formed atop already elevated base line, for instance, in spring of 2007 (Fig. 2). The magnitude of the multiday peaks was generally greater than that of spikes.
Fig. 2. Time series of daily mean N\textsubscript{2}O fluxes (open circles), air temperature (gray solid line), rainfall (gray bars), and soil moisture content (open triangles) monitored at Harford T&R Center in 2006 to 2009. Horizontal lines indicate annual 75th percentile (solid), mild outlier fence (dashed), and extreme outlier fence (dotted-dashed) for N\textsubscript{2}O data. Vertical line separates measurement data from fields A (2006) and B+C (2007-2009).
The majority of multiday peaks were observed during March–April and July–August in all categories. Those most prominent and long-lasting occurred on 4 to 12 July 2006; 25 Mar. to 24 Apr. 2007; 3 to 22 Apr. 2008; 15 to 20 July 2008; 11 to 19 Mar. 2009; and 27 to 31 May 2009 (Fig. 5). Within those periods, multiday peaks were sometimes separated by one or several low-flux days.

Spikes in the 75th percentile category were more evenly distributed along the annual timescale, and were observed nearly every month in 2006 to 2009. They were, however, less frequent during the late fall and winter. Spikes in the mild categories occurred in August (three in 2006 and one in 2007), with one of the August 2006 spikes also crossing the extreme threshold.

The Effect of Environmental Factors on Potential Nitrous Oxide Hot Moments

Environmental Factors: Temperature, Rainfall, and Soil Moisture

In 2006 to 2009, daily air temperatures varied from –19°C in January 2009 to 28°C in June 2008 (Fig. 2). Monthly growing season and annual mean temperatures were close to the 30-yr normal for the region. The exceptions were July 2006 (22°C vs. the monthly normal mean of 20°C), February 2007 (–8°C vs. monthly normal mean of –4°C) and January 2009 (–9°C vs. the monthly normal mean of –5°C).

The fluctuations in daily mean temperature (rate of change 2−5°C per day) lasting for up to 10 d, were most frequent in March and April of the monitoring period (Fig. 5). Occasional temperature pulses also occurred in 2 to 7 July 2006 (8°C) and 3 to 8 Jan. 2008 (abnormally large fluctuation of 31°C). Soil temperature (measurements started midsummer 2007) generally followed air temperature cycles in the warmer months ($R^2 = 0.91$), but often remained above or around 0°C, even when associated air temperatures dropped below freezing ($R^2 = 0.43$).

Along with the warmest temperatures, the growing season of 2006 was characterized by abundant rainfall, with 700 mm from April to October. For 2007 to 2009, rainfall levels were close to the 30-yr normal both for the growing season (454 mm) and annual means (930 mm). The peak rainfall months were June and July of each year.

Heavy rains in summer 2006 resulted in the highest soil moisture content during the study period, 79 to 91% water-filled pore space (WFPS) from June to August (Fig. 2). In 2007 to 2009, soil moisture conditions were stable from November to January of each year, with the greatest annual WFPS (65–68%). Decreases in soil moisture attributed to winter soil freezing were documented in February (45% WFPS, the lowest observed value) of each year; and increases in WFPS up to 60% related to the spring soil thaw occurred in March and April. Brief pulses were infrequent and changes in soil moisture status were primarily gradual.

Table 2. Descriptive statistics for the annual and growing season N$_2$O emissions from the two N$_2$O-monitored sites, in Harford, NY (42°25’34“ N, 76°13’36“ W).

<table>
<thead>
<tr>
<th>Year</th>
<th>Site (crop)</th>
<th>N$_2$O-N flux</th>
<th>CV</th>
<th>Days of observations (n)</th>
<th>Eddy covariance data coverage</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Annual mean (median)</td>
<td>Growing season, Apr.–Oct. mean (median)</td>
<td>Min</td>
<td>Max</td>
</tr>
<tr>
<td>2006 (Apr.–Oct.)</td>
<td>A (alfalfa)</td>
<td>–</td>
<td>3.9 (2.4)</td>
<td>–2.9</td>
<td>39.7</td>
</tr>
<tr>
<td>2007</td>
<td>B+C (both corn)</td>
<td>2.3 (1.3)</td>
<td>2.5 (1.7)</td>
<td>–5.4</td>
<td>39.3</td>
</tr>
<tr>
<td>2008</td>
<td>B+C (corn+alfalfa)</td>
<td>1.4 (0.7)</td>
<td>1.6 (1.2)</td>
<td>–6.2</td>
<td>17.3</td>
</tr>
<tr>
<td>2009 (Jan.–May)</td>
<td>B+C (corn+alfalfa)</td>
<td>2.1 (1.3)</td>
<td>–</td>
<td>–6.7</td>
<td>17.3</td>
</tr>
</tbody>
</table>

Fig. 3. Histograms of annual N$_2$O fluxes.
Combined Effect of Environmental Factors on Nitrous Oxide Peak Events

The occurrence of N\textsubscript{2}O potential hot moments (both spikes and multiday peaks) was analyzed with respect to the environmental conditions: temperature, precipitation, and soil moisture (Fig. 6). The results are reported below as a percentage of total documented peak events for 75th percentile, the mild and extreme outlier categories, respectively. Overall, temperature rise appears to be the strongest environmental factor triggering the peak events, especially for the multiday peaks: 79, 83, and 84% of multiday N\textsubscript{2}O peaks were observed within 1 to 2 d after rapid increases in the air temperature (2–8°C). Increases in soil moisture (3–5% WFPS) preceded 41, 50, and 64% of total multiday peaks. The impact of precipitation was less obvious: only 34, 29, and 40% of multiday peaks followed rainfall events (>5 mm) and only after prolonged dry periods (>7 d). The effect of combined environmental changes on the appearance of multiday peaks was also analyzed: 23, 25, and 28% of multiday peaks followed changes in all three parameters; 32, 27, and 36% appeared to be affected by temperature and rainfall shifts; and 38, 46, and 56% of total multiday peaks responded to combined changes in the temperature and soil moisture.

Spikes were more independent of changing environmental conditions than multiday peaks (Fig. 4b). In the 75th percentile category, 47% of spikes were not linked to measured environmental parameters, whereas 33, 23, and 18% followed temperature increase, rainfall events and soil moisture rise, respectively. All spikes in the mild and extreme outlier category responded to temperature rise and, in one case, combined changes in all three parameters.

The Effect of Manure Applications and Soil Mineral Nitrogen on Nitrous Oxide Peak Events

The seasonal trend in soil NO\textsubscript{2}/NO\textsubscript{3}–N showed maximum concentrations at the same time or immediately after manure application months: July 2006, January to March 2007, and January to April 2008 (Fig. 7). A gradual concentration decrease by the end of a growing season likely was due to the active crop N uptake and leaching. Crop harvest and consequently terminated N plant uptake resulted in the small rise in October to November of each year. Soil NO\textsubscript{2}/NO\textsubscript{3}–N concentrations also reflected the differences in the annual amounts of applied manure N.

Due to the low frequency of soil sampling, a day-to-day comparison between individual N\textsubscript{2}O peak events and mineral soil N content was not possible; however the effect on the occurrence and magnitude of N\textsubscript{2}O peak events was noticeable even at the monthly and seasonal scale. The majority of N\textsubscript{2}O multiday peaks were observed when the soil N contents were the greatest (Fig. 6). Monthly average N\textsubscript{2}O peak values also were moderately well correlated with the NO\textsubscript{3}/NO\textsubscript{2}–N soil concentrations ($r^2 = 0.60$, not shown on the figure).

**DISCUSSION**

Studies of agricultural N\textsubscript{2}O emissions often focus on the analysis of correlations between continuous time series of N\textsubscript{2}O fluxes and individual environmental factors, such as N availability, soil moisture, and temperature, as those factors are used for N\textsubscript{2}O predictions and modeling. Common understanding is that (i) approximately 1% of added N converts to the N\textsubscript{2}O-N emitted to the atmosphere, (ii) the soil moisture content within 60 to 90% WFPS range favors denitrification, a major mechanism

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**Table 3. Annual distribution and cumulative emission contributions of N\textsubscript{2}O peak events using three threshold values for potential hot moments. Mild and extreme outlier thresholds were set at 1.5 and 3 times the inter-quartile range, respectively, for each corresponding year.**

<table>
<thead>
<tr>
<th>Year</th>
<th>N\textsubscript{2}O-N peak event threshold value, mg m\textsuperscript{-2} d\textsuperscript{-1}</th>
<th>Total number of above-threshold N\textsubscript{2}O peak events</th>
<th>Percentage of cumulative annual emission contributed by N\textsubscript{2}O peak events</th>
<th>Percentage of total timeframe covered by N\textsubscript{2}O peak events</th>
<th>Avg. percentage of total emissions covered by a single peak</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>75th%</td>
<td>Mild</td>
<td>Extreme</td>
<td>75th%</td>
<td>Mild</td>
</tr>
<tr>
<td>2006</td>
<td>4.8</td>
<td>10.7</td>
<td>16.7</td>
<td>21</td>
<td>6</td>
</tr>
<tr>
<td>2007</td>
<td>3.4</td>
<td>8.8</td>
<td>14.3</td>
<td>82</td>
<td>21</td>
</tr>
<tr>
<td>2008</td>
<td>2.8</td>
<td>7.5</td>
<td>12.2</td>
<td>77</td>
<td>20</td>
</tr>
<tr>
<td>2009</td>
<td>3.1</td>
<td>7.1</td>
<td>11.1</td>
<td>31</td>
<td>10</td>
</tr>
</tbody>
</table>
contributing to \( \text{N}_2\text{O} \) soil emission, and (iii) the flux response increases with increasing temperature, generally following the Arrhenius function (Bateman and Baggs, 2005; Holtan-Hartwig et al., 2002; IPCC, 2006; Smith et al., 2003, 1998). However, complex interactions between those factors and often disproportional flux response make empirical relationships among them difficult to establish.

The tendency of \( \text{N}_2\text{O} \) fluxes to form episodic peaks that contributed a high fraction of the cumulative emissions within short timeframes has been described previously (Kroon et al., 2007; Parkin and Kaspar, 2006; Scanlon and Kiely, 2003). We observed similar trends in our study, with approximately half of measured emissions coming from short seasonal outbursts of \( \text{N}_2\text{O} \) activity and near-background fluxes throughout the rest of the year. This behavior of \( \text{N}_2\text{O} \) flux meets the general definition of hot moments, first suggested for biogeochemical processes by McClain et al. (2003) and further developed for \( \text{N}_2\text{O} \) emissions from denitrification by Groffman et al. (2009). Based on that definition, the \( \text{N}_2\text{O} \) hot moment can be described as a brief flux peak event formed in response to the confluence of critical environmental factors. Our study is the first effort to analyze a long-term dataset of daily \( \text{N}_2\text{O} \) fluxes, focusing on individual peak events exceeding certain thresholds as potential hot moments characterizing their frequency, magnitude and contribution to the cumulative flux, and the combined triggering effects of soil moisture, temperature, rainfall, and soil N availability.

Challenges in hot moment quantification are related to the fact that there is no agreed-on operational definition of a hot moment, and the magnitude and time scale of \( \text{N}_2\text{O} \) flux events are highly variable even among similar crop, climate, or soil types. Any categorization of \( \text{N}_2\text{O} \) flux absolute values therefore is indeed relative, and in most cases only appropriate for fluxes within the same dataset or specific measurement range. Higher frequency of measurements improves quality of the analysis based on the hot moment approach; however, resolution scale has to be adjusted to the study timeframe and data aggregation. We monitored \( \text{N}_2\text{O} \) fluxes over multiple annual agricultural cycles and accumulated more than 3 yr of half-hour EC flux data. Averaging 12 to 48 half-hour \( \text{N}_2\text{O} \) fluxes to the daily means helped to reduce high data density and facilitated comparisons with the majority of long-term observations reported in literature, while still reflecting changes in the daily emission levels.

The basic step in the analysis is establishing a numerical threshold above which a given \( \text{N}_2\text{O} \) flux event can be considered a hot moment. We suggest using statistical thresholds to link the threshold values to the flux measurement range and the box plot method to determine whether \( \text{N}_2\text{O} \) hot moments can be treated as statistical outliers. Three threshold categories were compared. Peak events in the mild and extreme outlier categories were less frequent than in the 75 percentile category, and covered a much shorter timeframe, but the contribution to the total flux from a single outlier event was up to two to three times greater than an event in the 75th percentile category. The peak event contribution and covered timeframe in the mild outlier category were the least variable between years and showed the best agreement with the results of Scanlon and Kiely (2003) and Parkin and Kaspar (2006).

The temporal/seasonal patterns of key environmental conditions preceding peak events were analyzed to determine whether said peaks qualified as hot moments and which peak threshold best represented hot moment potential. Most pronounced of all was the triggering effect of abrupt temperature pulses, as up to 85% of total multiday \( \text{N}_2\text{O} \) peaks followed warming events within 1 to 2 d. Changes in soil moisture content were the second most important factor of influence, followed by up to 64% of \( \text{N}_2\text{O} \) peak events. Rainfall had the least total impact, as it only triggered peak events after a long dry period or/and by causing a measurable change in the soil moisture status. A given parameter’s rate of change was more important for triggering an emission peak than its absolute value. This triggering effect, however, only worked under certain pre-existing conditions: the extent of change should take place when all factors of influence stay within the range favorable for \( \text{N}_2\text{O} \) production. Figure 5 illustrates the examples of immediate \( \text{N}_2\text{O} \) response to the abruptly changing temperature. The peak events followed the temperature “triggers” when a combination of flux-promoting conditions occurred: warm drying–rewetting in 2006 (\( T^\circ \text{C} \leq 20^\circ \text{C}, 60\% \leq \text{WFPS} \leq 90\%, \text{high N availability} \)), or freezing– thawing in 2007 to 2009 (\( 0 \leq T^\circ \text{C} \leq 10^\circ \text{C}, 60\% \leq \text{WFPS} \leq 90\%, \text{high N availability} \)). Our study thus confirms that the outburst of \( \text{N}_2\text{O} \) activity is driven by both the convergence of environmental factors as “reactants” (Groffman et al., 2009; McClain et al., 2003), and the pre- and post-event conditions impacting soil transport properties and/or microbiological status (Matzner and Borken, 2008; Wagner-Riddle et al., 2007).

The dependence of \( \text{N}_2\text{O} \) peak events on seasonal changes in temperature and soil moisture determined two annual trends that were particularly well pronounced for the peak events in the outlier categories. One was observed during intense summer rainfalls, for example, in summer 2006, where the combination of an abrupt increase in soil moisture under warm temperatures caused increased \( \text{N}_2\text{O} \) evolution. The second trend was typical for early spring (2007-2009) when spring thaw caused rapid and dramatic changes in both soil moisture and temperature. In both cases, recent N fertilization increased the magnitude of peak events, even though it did not produce them independently. For

**Table 4. Distribution of \( \text{N}_2\text{O} \) multiday peaks and spikes by the year using three threshold values for potential hot moments.**

<table>
<thead>
<tr>
<th>Year</th>
<th>Number of ( \text{N}_2\text{O} ) multiday peaks</th>
<th>Number of ( \text{N}_2\text{O} ) spikes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>75th%</td>
<td>Mild</td>
</tr>
<tr>
<td>2006</td>
<td>12</td>
<td>3</td>
</tr>
<tr>
<td>2007</td>
<td>52</td>
<td>20</td>
</tr>
<tr>
<td>2008</td>
<td>46</td>
<td>20</td>
</tr>
<tr>
<td>2009</td>
<td>23</td>
<td>9</td>
</tr>
<tr>
<td>Total</td>
<td>133</td>
<td>52</td>
</tr>
</tbody>
</table>
Fig. 5. Close-up plots of the peak events in 2006 to 2009 (open circles–N₂O flux; open squares– soil moisture content; black and gray dots–air and soil temperature, respectively; black and gray bars–rainfall and applied manure N, respectively; solid, dashed and dotted-dashed horizontal lines–75th percentile, mild and extreme outlier thresholds, respectively).
instance, N$_2$O peak events with lower magnitudes occurred in spring 2009 even without recent manure application.

Overall, multiday peaks in the mild outlier category showed the best agreement with the definition of a hot moment, as it was the lowest threshold category in which a majority of peak events responded to the environmental changes and formed the most distinct seasonal patterns that were observed across multiple years. The relative timeframe and cumulative N$_2$O emission contributions of peak events in that category were consistent from year to year among similar field treatments and were also consistent with previous studies (e.g., Scanlon and Kiely, 2003). The extreme outlier category demonstrated similar trends but likely underestimated the peak event occurrence and emission contribution. In contrast to both outlier categories, the 75th percen-
tile peak events contained a substantial fraction of unexplained spikes not related to the soil moisture and temperature status and covered longer timeframes with smaller individual flux contributions. The uncertainty introduced by those spikes could be caused by various factors not analyzed here, and remains a task for future research.

Exploration of N2O hot moment quantification criteria and temporal distribution patterns needs to continue, with particular attention to the interplay of peak event triggers. In particular, the analysis of the most contributing emission events and environmental data at higher temporal resolution could provide useful insight into the time and mechanism of N2O response. Continuous high-frequency N2O flux monitoring and quality-assured data are essential for such studies.

CONCLUSIONS
Our long-term study of N2O emissions from manure fertilized fields in New York State indicated that up to a half of the annual N2O emission was generated in form of the event-induced peak fluxes above specific thresholds. Most contributing emissions were formed as multi-day N2O peak events resulting from summer precipitation or early spring thaws. They represented strong repetitive seasonal patterns of high intensity N2O events responding to a combination of environmental factors of influence, and thus were defined as hot moments. The availability of manure N determined the potential intensity of hot moments, whereas abrupt weather events such as changes in soil moisture and temperature were the major hot moment triggers. Hot moment analysis therefore could be a promising tool for estimating and predicting the most productive N2O events, especially when direct correlations between individual parameter time series are difficult to determine. More continuous high-resolution N2O flux and environmental data are needed for both quantification and refining criteria of hot moment estimates.

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REFERENCES


