

## Ecosystem-scale measurements of nitrous oxide fluxes for an intensely grazed, fertilized grassland

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[1] An eddy covariance (EC) system with a tunable diode laser trace gas analyzer was used in a field setting in Ireland to measure  $N_2O$  emissions on a continuous basis over an eight-month period, spanning a range of seasonal conditions. Intensely-grazed grassland fields within the footprint area of the EC sensors were subject to chemical fertilizer and slurry applications in order to boost grassland yield, and the amounts of these applications were documented by the farmers on a monthly basis. Three major emission events, covering a timeframe of 16 days (6.6% of the measurement period) contributed to over half (51.1%) of the observed cumulative flux. Two of these events occurred during the summer, while the third occurred during the winter, with vastly different soil moisture and soil temperature conditions associated with these times of the year. The type of N applications (fertilizer vs. slurry), soil moisture and temperature status had implications for controlling the short-term rates of  $N_2O$  emissions. Cumulative  $N_2O$  emissions, however, were driven by fertilizer and slurry N applications, as the emission factor of approximately 3.0% displayed consistency throughout the eight-month period. **INDEX TERMS:** 0315 Atmospheric Composition and Structure: Biosphere/atmosphere interactions; 1615 Global Change: Biogeochemical processes (4805); 1866 Hydrology: Soil moisture. **Citation:** Scanlon, T. M., and G. Kiely, Ecosystem-scale measurements of nitrous oxide fluxes for an intensely grazed, fertilized grassland, *Geophys. Res. Lett.*, 30(16), 1852, doi:10.1029/2003GL017454, 2003.

### 1. Introduction

[2] Fertilizer N applications to grasslands are often required in order to achieve optimum yields, however a byproduct of this increasingly widespread agronomic practice is atmospheric pollution in the form of nitrous oxide ( $N_2O$ ) emissions. This trace gas is implicated in the destruction of stratospheric ozone [Crutzen, 1976] and acts as a greenhouse gas [Pranther *et al.*, 1995], making essential the collection of inventories and the development of a refined understanding of the processes that regulate  $N_2O$  emissions. This is especially important for ecosystems where  $N_2O$  emissions are greatly amplified on a per unit area basis by routine additions of fertilizer N, such as the grassland system examined in this paper. We present micrometeorologically-based  $N_2O$  flux measurements that capture the dynamics of these emissions over sub-daily to seasonal timescales.

[3] Chamber measurements have thus far provided the vast majority of the information obtained on soil fluxes of

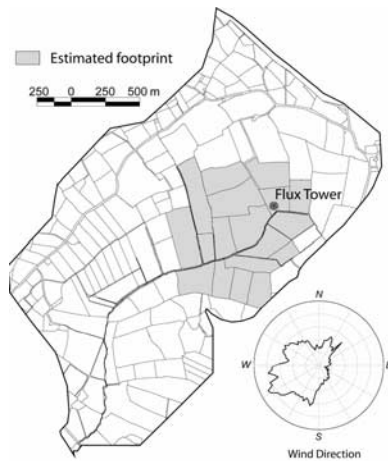
$N_2O$ . The high degree of spatial and temporal variability known to be associated with these fluxes can be accommodated for by a sampling program that involves regular, intensive monitoring of numerous chambers. Indeed, studies of this type have provided benchmark assessments of grassland and agricultural  $N_2O$  emissions [e.g., Bouwman, 1996; Dobbie *et al.*, 1999; Groffman *et al.*, 2000]. Chamber measurements are also useful for the purposeful manipulation of the factors affecting nitrification and denitrification rates, thereby isolating the processes involved in  $N_2O$  production [e.g., Harrison *et al.*, 1995; Yamulki *et al.*, 1998; Abbasi and Adams, 2000]. Drawbacks do exist, however, in terms of how representative the chambers are of the overall landscape-level ecosystem function. For instance, in the case of the intensively-grazed grassland examined in this study, the top-down controls on grass production as well as the effects of incidental fertilization via animal excreta may not be adequately represented within the chamber plots.

[4] An alternative strategy for measuring  $N_2O$  emissions is the employment of micrometeorological methods, which intrinsically provide area-integrated, continuous coverage of the soil-atmosphere exchange. Within the last decade, tunable diode laser (TDL) spectroscopy has developed as a technique to measure  $N_2O$  concentrations in a fast-response, high precision manner suitable for eddy covariance (EC) methodological requirements [Zahniser *et al.*, 1995], although to date field implementations have generally focused on method evaluation and have been of short duration [e.g., Christensen *et al.*, 1996; Hargreaves *et al.*, 1996; Laville *et al.*, 1999]. Only recently have TDL systems been introduced that show promise for long-term EC field applications [Edwards *et al.*, 2003].

[5] In this paper, we present the results from the first eight months of a planned long-term study in which a TDL is used as part of an EC system to measure  $N_2O$  fluxes over a fertilized grassland. Continuous measurements of this kind are of interest for establishing more robust relationships between the amount of fertilizer N added and the magnitude of  $N_2O$  emitted from the grassland ecosystem [Groffman *et al.*, 2000]. An additional, perhaps more significant goal of this research is to gain insight into the factors (i.e., soil moisture, soil temperature, soil N availability) that control the dynamics of  $N_2O$  emissions through the temporally intensive monitoring of the EC fluxes under transient environmental conditions.

### 2. Site Description and Methods

[6] The setting for this research is an intensively-grazed grassland ecosystem near the town of Donoughmore in Co.



**Figure 1.** Map of the catchment area in which the eddy covariance study of N<sub>2</sub>O emissions took place. The shaded fields indicate those estimated to be within the flux footprint, based in part on the observed probability distribution function of the wind direction (inset).

Cork, Ireland. Average rainfall for this location is approximately 1470 mm/year. Ryegrass is the primary vegetation cover, and the soil types are defined as peaty podzols and brown podzolics. Like much of the surrounding rural area, the landscape near the N<sub>2</sub>O flux tower is partitioned into small fields that define the range boundaries for individual cattle herds that are used for dairy and beef production.

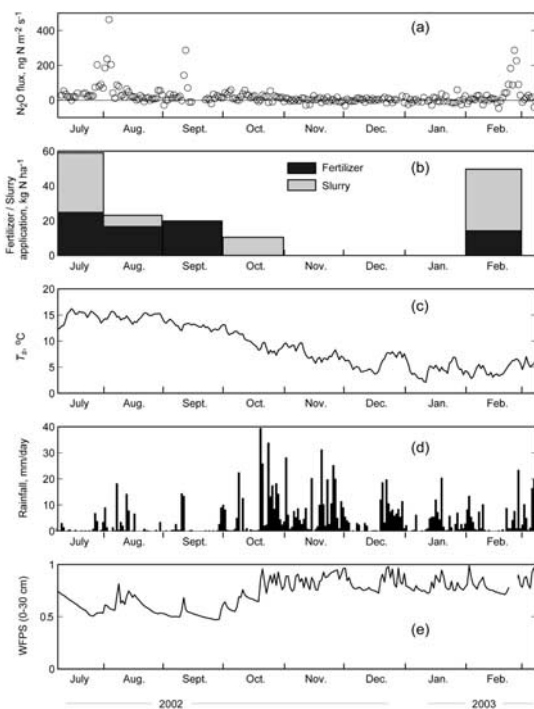
[7] The patchwork landscape plays a significant role with regard to interpreting the EC measurements, as numerous fields are contained within the footprint of the sensor. The fields estimated to be within this general footprint area were identified according to fetch to sensor height (6 m) ratio of 100:1, combined with information from the probability density function of the wind direction (Figure 1). Since multiple landowners operate within the footprint area, asynchronous additions of fertilizer and slurry, in various amounts, took place as management strategies for boosting grassland production varied according to the individual farmers. Monthly surveys completed by the farmers reported the amounts and types of fertilizer, as well as the quantities of manure/urine-based liquid slurry, that were added to the fields. Area-weighted values of N additions within the footprint area were derived on a monthly basis.

[8] The EC system consisted of a 3-D sonic anemometer (Campbell Scientific Inc., model CSAT3) paired with a TDL trace gas analyzer (Campbell Scientific Inc., model TGA100), which uses a reference gas to maintain continuous calibration. Data from each were logged at a frequency of 10 Hz, and the lag time for the air traveling through the 9.5-m tube from the location of the sonic anemometer to the trace gas analyzer was assumed to correspond to the peak in the lag correlation between the two time series. Reynolds-averaged EC fluxes were computed on a half-hour basis. No high or low frequency filtering was used and the anemometer data exhibited no discernible angular offset to warrant coordinate rotation. Eight months of flux data were recorded, starting on July 9, 2002 and extending through March 9, 2003. In an effort to discard outlier half-hour flux values in an unbiased manner, only two selection criteria were used. The first looked for unsteady means in the

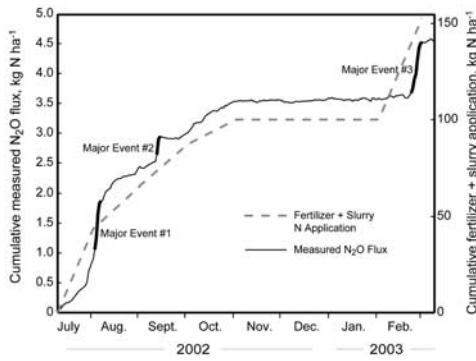
vertical wind speed, which eliminated 6.2% of the half-hour fluxes, and the second looked for abnormally large products of the standard deviations for vertical wind speed and N<sub>2</sub>O concentration, which eliminated 3.2% of the flux measurements (some of these occasions overlapped). Factoring in instrument down-time along with the elimination of these data points resulted in “good” data for 90.4% of the eight-month time series. Noise on the half-hour EC flux measurements, which was often greater than the flux magnitude during periods of low N<sub>2</sub>O emissions, was approximately Gaussian and was therefore reduced through averaging the half-hour values over daily time steps. If less than 12 half-hour values were available for a given day, then the daily average flux was linearly interpolated from neighboring values. Other environmental parameters measured concurrently were soil temperature at a depth of 7.5 cm, soil moisture averaged over a depth of 0–30 cm (Campbell Scientific Inc., model CS615), and precipitation.

### 3. Results and Discussion

[9] Emissions of N<sub>2</sub>O from soils are notoriously variable in both space and time. With the employment of the EC technique, the spatial variability of the fluxes collapse into a single integrated average, while the temporal variability of the fluxes is captured in full. Figure 2a shows the daily time series of average N<sub>2</sub>O fluxes measured at the fertilized grassland site over a period of eight months. For the most part, the mean daily fluxes were low (<30 ng N m<sup>-2</sup> s<sup>-1</sup>), but there were several instances in which the emission rates became elevated by over an order of magnitude from back-



**Figure 2.** Eight-month time series of measurements for (a) average daily N<sub>2</sub>O flux, (b) monthly fertilizer and slurry applications, (c) average daily soil temperature at a depth of 7.5 cm, (d) daily rainfall, and (e) average daily soil moisture over a depth of 0–30 cm.



**Figure 3.** Cumulative measured  $\text{N}_2\text{O}$  flux and fertilizer/slurry N applications. The left axis is scaled to 3.0% of the right axis.

ground levels. Also shown for this time series are the monthly rates of fertilizer and slurry applications (Figure 2b), soil temperature ( $T_s$ ) (Figure 2c), daily rainfall totals (Figure 2d), and water-filled pore space (WFPS) (Figure 2e). Note that the instances of peak  $\text{N}_2\text{O}$  emissions correspond with the general timing of select rainfall events. Like the results reported for greenhouse chamber experiments [Smith *et al.*, 1998], the peak emissions in this field setting do not occur at the times of fertilization, but rather later on with the chemical and physical breakdown of the fertilizer by rainfall, the vertical transport of this available N to the subsurface, and the wetting of the soils.

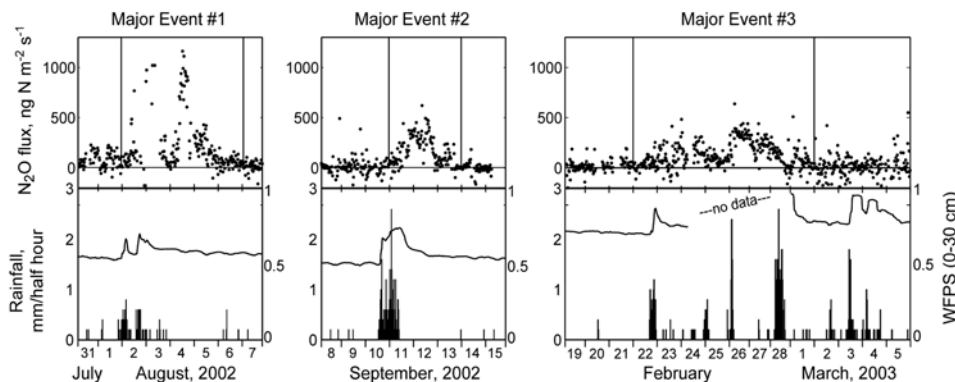
[10] Both the processes of nitrification and denitrification can lead to the release of  $\text{N}_2\text{O}$  as a byproduct. Increased  $\text{N}_2\text{O}$  emissions following rainfall events, as seen in many studies in various settings, suggests that the anaerobic process of denitrification is comparatively dominant with respect to producing these emissions. Following this premise, researchers working with fertilized systems have reported positive correlations between  $\text{N}_2\text{O}$  fluxes and WFPS [e.g., Dobbie *et al.*, 1999; Weitz *et al.*, 2001], and between  $\text{N}_2\text{O}$  fluxes as a function of WFPS and  $T_s$  [e.g., Skiba *et al.*, 1998; Smith *et al.*, 1998], since soil temperature is relevant in affecting the kinetics of the microbial processes. Similar relationships for the data presented in Figure 2 would not be definitive since large flux events are observed during periods with low WFPS and high  $T_s$  (July, Aug., Sept.) as well as during periods with high

WFPS and low  $T_s$  (Feb.). Limitations on the  $\text{N}_2\text{O}$  fluxes by WFPS and  $T_s$  appear to be secondary to the limitations imposed by N availability.

[11] Additions of N to the grassland fields in the form of fertilizer and slurry drive the emissions of  $\text{N}_2\text{O}$ , a point that can be best illustrated by examining their respective cumulative inventories. These results are shown in Figure 3 where it is assumed, based on a lack of more detailed information, that the fertilizer and slurry applications are spread evenly throughout each month. The similarities in the shapes of the curves are evident, and the relative scales of the axes reveal that approximately 3.0% of the N added to the grassland is lost to the atmosphere in the form of  $\text{N}_2\text{O}$ . This emission factor is on the high end, but within the range of the grassland emissions factors surveyed by Dobbie *et al.* [1999]. Several pulses of  $\text{N}_2\text{O}$  emissions, labeled as Major Events #1–3 in Figure 3, contribute to over half (51.1%) of the eight-month cumulative flux, yet cover a total timeframe of only 16 days (6.6% of the time).

[12] The three major flux events highlighted in Figure 3 are shown in half-hour detail in Figure 4. One notable observation is the 1–2 day time lag between the soil WFPS peak and the  $\text{N}_2\text{O}$  pulse, an effect that has been documented elsewhere [e.g., Smith *et al.*, 1998] and which, incidentally, confounds any relationship that can be drawn between  $\text{N}_2\text{O}$  flux and WFPS at these short timescales. This lag phenomenon could possibly be attributed to physical diffusion of gas through the soil or controls by microbial growth rates in defining the size of the denitrifier pool.

[13] An interesting contrast exists between the characteristics of the  $\text{N}_2\text{O}$  pulses observed for Major Events #1 and #3 (Figure 4). Both of these events occurred at the end of months (July for ME #1, February for ME #3) that had similar magnitudes of fertilizer and slurry applications (Figure 2), yet the ambient conditions for  $T_s$  and WFPS were quite different for these summer and winter periods, respectively. The cumulative  $\text{N}_2\text{O}$  fluxes for the two events are nearly identical (Figure 3), yet the summertime event was characterized by abrupt, highly-elevated peaks in  $\text{N}_2\text{O}$  emissions, while the wintertime event was more continuous, long-lasting, and subdued in terms of peak rates. These observations can be interpreted by adopting a modified “hole-in-pipe” (HIP) conceptual model [Firestone and Davidson, 1989; Davidson, 1991], in which rates of nitrification and denitrification can be thought of as the flow



**Figure 4.** Half-hour data for the three major  $\text{N}_2\text{O}$  flux events. Vertical lines bounding the flux measurements define the 16 days that contribute to more than half of the cumulative flux that was measured over the eight-month period.

through a pipe and the  $N_2O$  emissions thought of as leakage through holes, the size of which are determined by WFPS (nitric oxide, a part of the original HIP model, is not considered in the present context). An addition to the conceptual model would be  $T_s$ , which acts as a valve on the pipe, thereby regulating the rate of flow. The soil temperature is high for ME#1, meaning that the flow through the pipe proceeds at a fast rate, allowing  $N_2O$  to be lost to the atmosphere in large bursts. For ME#3, the flow is more restricted by  $T_s$ , so the  $N_2O$  emissions proceed at a much slower rate. The overwhelmingly dominant factor in both cases is N availability, which is analogous to the volume of the reservoir that drains through the pipe. Due to the similarities in reservoir volumes for ME#1 and ME#3, the cumulative fluxes are similar. This reservoir is, of course, subject to losses by plant uptake and leaching, and year-to-year variability in emission factors for individual sites are sensitive to the interplay between these loss rates, the reservoir volume, and the rate of "flow".

[14] Finally, the form of N additions to the grassland fields can also affect the rate of flow in the HIP model. Laboratory experiments have shown that emissions from slurry applications proceed more gradually than those deriving from fertilizer applications [Williams *et al.*, 1998]. Slurry contains N that is almost exclusively in the form of  $NH_4^+$  which must first undergo nitrification before proceeding to the denitrification process, while the fertilizers are mostly  $NH_4^+-NO_3^-$  based and can therefore undergo nitrification and denitrification simultaneously [Abbasi and Adams, 2000]. For the month of October, only slurry was added to the fields (Figure 2b), and although there were no major emission events during this month (Figure 2a), the cumulative flux was greatly influenced by the persistence of elevated emissions (Figure 3). While there is no convincing evidence that the type of N applications affect the cumulative  $N_2O$  emissions, the temporal dynamics of the emission rates do appear to be affected.

#### 4. Summary

[15] The EC flux measurements presented here cover the first eight months of a planned long-term study of  $N_2O$  emission rates in a setting that is typical of intensely grazed, managed grasslands that cover approximately 45% of Ireland's total land area. Availability of N from fertilizer and slurry applications was the most important factor for driving the losses of N to the atmosphere in the form of  $N_2O$ , with the emission factor remaining relatively constant and independent of seasonal conditions. This lends support to Bouwman *et al.*'s [2002] model of  $N_2O$  emission factors that considered site-specific descriptors such as crop type, soil texture, soil pH, and soil organic carbon content, while neglecting temporal information pertaining to the timing of fertilizer applications in relation to rainfall and soil temperature variability. Ongoing and future data collection at this site should help to facilitate our assessment of this and build on our current understanding of  $N_2O$  emission processes.

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