

Field Nitrogen Losses Induced by Application Timing of Digestate from Dairy Manure Biogas Production

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Abstract

Anaerobic digestion of dairy manure has environmental benefits, but the impact of effluent (i.e., digestate [DG]) application on environmental nitrogen (N) losses from soils has not been well quantified. Our objective was to evaluate how field application of DG affected nitrous oxide (N_2O) emissions and nitrate (NO_3) leaching compared with raw dairy manure (RM) in spring versus fall applications. We measured N losses year-round for 2.5 yr in silage corn on tile-drained clay soil in Alfred, Ontario, Canada. Treatments were: digestate applied in spring (DS) and fall (DF), raw dairy manure applied in spring (RS) and fall (RF), urea applied in spring, and a control. Overall, the source of N had no effect on annual N_2O emissions (overall average DG and RM, $4.9 \text{ kg N}_2\text{O-N ha}^{-1} \text{ yr}^{-1}$), but more NO_3 leached from DS than RS treatments (8.8 and $4.8 \text{ kg NO}_3\text{-N ha}^{-1} \text{ yr}^{-1}$ on average, respectively). Estimated indirect N_2O emissions from leached $\text{NO}_3\text{-N}$ were small ($<0.2 \text{ kg N}_2\text{O-N ha}^{-1} \text{ yr}^{-1}$). Timing of application did not affect annual N_2O emissions but did shift emissions to the non-growing season for fall applications (65% on average) and to the growing season for spring applications (60% on average). Overall environmental N losses ($\text{N}_2\text{O-N} + \text{NO}_3\text{-N}$) from DG were similar to RM when applied at the same time. For the conditions of our study, downstream emissions from anaerobic digestion (i.e., emissions induced by applied digestate) do not present an adverse trade-off to the environmental benefits incurred during the biogas production phase.

Core Ideas

- Biodigestion has environmental benefits, but N losses from soils are uncertain.
- Nitrous oxide emissions and NO_3 leaching were evaluated.
- Digested and raw manure had similar annual N losses.
- Application in spring had lower annual NO_3 losses than fall application.
- Soil emissions were not a trade-off to environmental benefits of biogas production.

ON-FARM ANAEROBIC digestion of dairy manure produces electricity from methane (CH_4) combustion, offsetting nonrenewable CO_2 emissions, and mitigates greenhouse gases (GHGs) from manure storages (Möller and Stinner, 2009), but the effect of digested material (i.e., digestate [DG]) on downstream GHG emissions is an area of uncertainty. From an agronomic standpoint, DG quality is comparable to synthetic fertilizers (Vaneeckhaute et al., 2013) due to the conversion of organic N to ammonium (NH_4) during digestion. Environmentally, however, changes in DG characteristics (less C, more mineral N, and higher pH) may alter the potential for N losses through leaching and gaseous emissions compared with raw manure. Few studies have investigated the effect of DG on nitrous oxide (N_2O) emissions or nitrate (NO_3) leaching after field applications (Clemens et al., 2006; Rodhe et al., 2015). Field evaluations of total N_2O emissions from DG are necessary for providing fertilizer-specific emission factors that can aid in more accurate GHG inventories and bioenergy life-cycle assessments (Carter et al., 2011; VanderZaag et al., 2011).

Nitrous oxide is a potent GHG and a major contributor to stratospheric ozone depletion (Ravishankara et al., 2009). Approximately 1% of the total N applied to agricultural fields can be lost directly from the soil as N_2O emissions (IPCC, 2006), and 10 to 80% can be lost to water sources (Carpenter et al., 1998). Leached NO_3 is an indirect GHG because a portion is converted to downstream N_2O emissions (IPCC, 2006). Thus, effective N management strategies that minimize N losses are essential for maintaining profitable agricultural production and may also reduce direct and indirect N_2O emissions.

There are few evaluations of total N_2O emissions based on simultaneous measurements of direct N_2O emissions and NO_3 leaching (e.g., Maharjan et al., 2014; Pappa et al., 2011). Most N_2O emission studies focus on direct N_2O losses from agricultural soils even though direct soil surface emissions, animal waste management emissions, and indirect emissions through leaching/runoff and volatilization contribute to the total agricultural N_2O source (Nevison, 2000). Indirect N_2O emissions from

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Abbreviations: DF, digestate applied in fall; DM, dry matter; DS, digestate applied in spring; EF, emission factor; $\text{Frac}_{\text{LEACH}}$, fraction of N applied that leached; GHG, greenhouse gas; IS, inorganic fertilizer (urea) applied in spring; RF, raw dairy manure applied in fall; RM, raw dairy manure; RS, raw dairy manure applied in spring; TAN, total ammoniacal nitrogen.

leaching and runoff are considered an important agricultural N_2O source (Nevison, 2000) but are rarely presented in N_2O emission studies. Although the IPCC (2006) emission factor for leaching and runoff (EF_3) has a large uncertainty (0.05–2.5%), it provides a method for estimating N_2O emissions from measurements of NO_3-N leached and has been used in other studies (Venterea et al., 2011).

Manure application timing (spring vs. fall) is considered an area for potential N_2O mitigation. Canadian dairy farms, for example, apply approximately 30% of their manure in the fall (Beaulieu, 2004). Fall applications have been linked to greater environmental N loss because the N is applied >7 mo before crop uptake and conditions during the non-growing season may be favorable for denitrification and leaching (Rochette et al., 2004). Furthermore, N_2O losses may be greater from fall applications because N_2O emissions during the winter months significantly contribute to annual emissions (Röver et al., 1998; Wagner-Riddle et al., 1997, 2008). However, year-round studies on N_2O emissions that capture winter and spring thaw fluxes—arising due to freeze and thaw cycles (Christensen and Tiedje, 1990)—are limited.

Moreover, in annual cropping systems, N application in the fall compared with the spring can enhance NO_3 leaching (Randall et al., 2003; van Es et al., 2006) and indirect N_2O emissions. A key factor affecting N leaching is the amount of drainage, which varies seasonally (Di and Cameron, 2002). Early spring and late fall often have high drainage flow due to greater precipitation and lower evapotranspiration. Thus, N applied in the fall may be more susceptible to losses compared with spring-applied N.

This study addresses the need to evaluate N_2O emissions and NO_3 leaching from two potential mitigation strategies: (i) application of DG, and (ii) timing of application. Our objectives were to determine how N_2O emissions and NO_3 leaching were influenced by applications of DG compared with raw dairy manure (RM) in spring versus fall applications on a tile-drained clay soil through year-round measurements.

Materials and Methods

Site Description and Experimental Design

A 2.5-yr (October 2011–May 2014) experiment was conducted in Alfred, ON, Canada (45.34° N, 74.55° W) on a tile-drained Bearbrook clay (72% clay, 26% silt) with 12 plots (100 m × 15 m) instrumented for drainage water collection. Average soil characteristics were: pH, 7.1; organic C, 2.7%; total C, 3.0%; total N, 2741 kg ha⁻¹; mineral N, 93 kg ha⁻¹; and cation exchange capacity, 30.1 cmol_c kg⁻¹. Average annual temperature was 6.6°C, with 920 mm precipitation (1981–2010 average) (Environment Canada, 2013). A weather station (Onset HOBO Micro Station Data logger) was installed in 2012, and the Ottawa Central Experimental Farm weather station (~75 km from the site) was used to gap-fill missing data.

Treatments were raw liquid dairy manure and DG applied in the fall of 2011 and 2012 (RF and DF, respectively) and RM and DG applied in the spring of 2012 and 2013 (RS and DS, respectively) (Table 1). Treatments were arranged in two randomized complete blocks. In addition, one plot in each block received spring-applied inorganic fertilizer (IS) (urea, 25.1–11.7–16.7, N–P–K) to provide a reference for comparison with the organic amendments (spring is when farmers typically apply urea). Two additional control plots did not receive N input to provide a reference of background N losses. Treatments were surface-applied (incorporated within 24 h) at the same target rate of available N (140 kg N ha⁻¹) using factors for total ammoniacal N (TAN) retention and organic N mineralization (Government of Alberta, 2008; OMAFRA, 2009). All plots were seeded to silage corn (Pioneer Hybrid P8906HR) at 81,545 seeds ha⁻¹ (76-cm row spacing). The plots had historically received organic amendments (i.e., manure). The most recent amendment was applied 1.5 yr before the study (spring 2010). In 2011 a cover-crop mix of oilseed radish, buckwheat, and white peas was grown and tilled in early fall.

Both RM and DG were obtained from a local dairy operation (150 lactating cows) with a 1000-m³ anaerobic digester (37°C)

Table 1. Application dates for each treatment including quantity applied, total Kjeldahl N (TKN), total ammoniacal N (TAN), total organic N (Org-N), and available N.

Application date	Treatment†	Quantity applied	N source‡			
			TKN	TAN	Org-N	Available N§
kg ha ⁻¹						
28 Oct. 2011	RF	76 m ³ ha ⁻¹	219	99	120	115 ± 12a
	DF	60 m ³ ha ⁻¹	216	122	94	127 ± 11a
23 May 2012	RS	75 m ³ ha ⁻¹	274	130	144	134 ± 12a
	DS	69 m ³ ha ⁻¹	292	151	142	148 ± 23a
30 Oct. 2012	IS	558 kg ha ⁻¹	140	140	0	140 ± 8a
	RF	80 m ³ ha ⁻¹	211	136	76	135 ± 20a
	DF	67 m ³ ha ⁻¹	240	138	102	143 ± 12a
27 May 2013	RS	90 m ³ ha ⁻¹	266	132	134	133 ± 17a
	DS	87 m ³ ha ⁻¹	275	141	134	139 ± 11a
	IS	558 kg ha ⁻¹	140	140	0	140 ± 7a

† DF, digestate applied in fall; DS, digestate applied in spring; IS, inorganic fertilizer (urea) applied in spring; RF, raw manure applied in fall; RS, raw manure applied in spring.

‡ Retention factors of 0.85 (fall) and 0.75 (spring) were used to calculate ammonium-N available the year after application (OMAFRA, 2009). A mineralization factor of 0.25 was used to calculate the amount of Org-N available the first year (Government of Alberta, 2008).

§ Mean and SD are shown based on measured application collected in four 0.5-m² pans placed in each plot during application. Letters indicate significant differences ($p < 0.05$) between treatment on each application date.

fed $13 \text{ m}^3 \text{ d}^{-1}$ of RM and $13 \text{ m}^3 \text{ d}^{-1}$ of rendering grease waste. For our study, RM was collected from the under-barn holding pit; DG was collected from an earthen digestate storage during mixing (October 2011) or directly from the digester (May 2012, October 2012, and May 2013). Composite samples were collected at application to determine the amount of manure (L ha^{-1}) and N (kg ha^{-1}) applied (Table 1). Due to fluctuations in the nutrient content of the manure and digestate, the amount of total available N applied often differed from the target application rate of 140 kg ha^{-1} .

Sampling and Analysis

Direct N_2O Emission Measurements

Sampling of N_2O flux occurred every 7 to 10 d until snow cover, after which sampling was performed one to two times per month due to increased efforts required under winter conditions. Fluxes were measured using non-flow-through, non-steady-state chambers (Rochette and Hutchinson, 2005) consisting of a polyvinyl chloride collar (0.45 m i.d., 0.20 m high) and a chamber (0.45 m i.d., 0.08 m high) with a vent tube and covered in reflective material. Two collars were placed on plot centerlines, between rows, and 40 m apart. At the time of sampling (usually mornings), chambers were fitted to collars, and bricks ($\approx 6 \text{ kg}$) were placed on chambers to ensure a seal. Headspace air samples (20 mL) were collected 0, 10, 20, and 30 min after deployment and transferred to 12-mL evacuated glass vials (Exetainer, Labco Ltd.). Concentration of N_2O (ppmv) was determined by a gas chromatograph (CP-3800, Varian Inc.). Flux ($\text{ng N}_2\text{O-N m}^{-2} \text{ s}^{-1}$) was calculated as

$$\text{Flux} = \frac{dc}{dt} \times \frac{v}{a} \times \frac{28}{44} \quad [1]$$

where dc/dt is the change in headspace concentration (dc , ppmv N_2O converted to $\text{ng N}_2\text{O m}^{-3}$) over time (dt , seconds), v is the headspace volume (m^3), a is the chamber area (m^2), and $28/44$ is the ratio of molecular weights to convert N_2O to $\text{N}_2\text{O-N}$. Linear and quadratic regressions were used to determine dc/dt ; if neither was significant ($p < 0.05$), dc/dt was set to zero. All dc/dt data were graphed and inspected visually. Chamber headspace was the sum of chamber and collar volumes. Collar volume was determined monthly by measuring the collar height above soil (or snow) at 15 grid points across the collar surface. Snow above the collar was carefully removed, so headspace volume was the chamber volume (snow was returned after sampling).

NO_3 Leaching Losses

Nitrate leaching was monitored from 23 May 2012 to 22 May 2014. A subsurface (0.9 m deep) tile drain was located in the center of each hydraulically isolated plot. Calibrated tipping buckets at the outflow of each drain (in a building adjacent to the field) were connected to a data logger (CR10X, Campbell Scientific) that calculated flow volumes (L). Peristaltic pumps (FPU401, OmegaFlex) collected flow-weighted composite water samples for $\text{NO}_3\text{-N}$ determination. Daily $\text{NO}_3\text{-N}$ leaching losses (mg d^{-1}) were calculated by multiplying daily $\text{NO}_3\text{-N}$ concentrations (mg L^{-1}) by drainage volumes (L).

Soil and Plant Sampling and Analysis

Composite soil samples (0–15 cm) were collected at six locations per plot in undisturbed soil between rows after N applications and through the growing season each year for analysis of inorganic N (NO_3 and NH_4) with a flow injection analyzer (Method 12-107-06-2-A and 12-107-04-1-B, Quikchem 8000+ Series, Lachat Instruments). Bulk density was measured two or three times per year.

On sampling days when the soil was not frozen, volumetric soil water content (%) was measured using a time domain reflectometer (Field Scout TDR 300, Spectrum Technologies Inc.) at three locations near each chamber (0–12 cm depth). Water-filled pore space (WFPS, %) was calculated from volumetric soil water content and bulk density (Linn and Doran, 1984).

Whole plant samples (2 m in center rows at three locations per plot) were collected at maturity in 2012 and 2013 to determine dry matter (DM) yield. A 1-g dried subsample was analyzed for total N by Kjeldahl digestion and colorimetric analysis (QuikChem 8500 Series 2, Lachat). Silage N yield was calculated by multiplying the total N concentration (%) by dry biomass yield (kg ha^{-1}).

Data Analysis

Data gaps were filled to enable annual losses of N_2O and NO_3 to be determined. Linear interpolation was used between N_2O sampling dates and to fill occasional short-flow data gaps. Gaps in NO_3 concentrations were filled with the previous sample if within 5 d (Hernandez-Ramirez et al., 2011; Ruark et al., 2009); a seasonal average was used for longer gaps.

Annual N_2O emissions and leached NO_3 were calculated by summing daily values over one full year after each N application, which was defined as a “treatment year.” Fall treatment years were 30 Oct. 2011 to 29 Oct. 2012 and 30 Oct. 2012 to 29 Oct. 2013. Spring treatment years were 23 May 2012 to 22 May 2013 and 23 May 2013 to 22 May 2014. Thus, fall and spring treatment years shared the same growing season but had a different non-growing season. Emissions from unfertilized control plots were subtracted before scaling annual N_2O emissions by N applied.

The fraction of N applied that leached ($\text{Frac}_{\text{LEACH}}$) was calculated as the $\text{NO}_3\text{-N}$ mass load minus the $\text{NO}_3\text{-N}$ leached from the control divided by the total N applied in that treatment year. Indirect $\text{N}_2\text{O-N}$ emissions used the calculated $\text{Frac}_{\text{LEACH}}$ multiplied by 0.0075 (EF_5) (IPCC, 2006), which has been used previously (Maharjan et al., 2014; Reay et al., 2009; Venterea et al., 2011).

A repeated measures ANOVA (PROC MIXED, SAS Institute, Cary, NC) with chambers as a nested variable tested for significant treatment effects on annual (i.e., treatment year) N_2O emissions for each organic amendment application timing (i.e., fall applications included DF and RF and spring applications included DS and RS). Fixed effects were year, N source (DG and RM), and timing (spring and fall) as well as the interaction terms; chambers within plots were considered a random effect. An autoregressive covariance structure was used in the model because it provided the best fit statistics. If a treatment effect on annual N_2O emissions was significant ($p < 0.05$), differences in least squares means were tested using the Tukey–Kramer method. Annual N_2O emissions from all treatments, including the control and inorganic treatment, were analyzed using a

separate repeated measures ANOVA. For leached NO_3^- , a paired t test was used to determine significant differences between spring versus fall applications (whereby DG and RM were combined) and between DG and RM (whereby spring and fall in Treatment Year 2 were combined).

Results and Discussion

Manure Characteristics

Compositions of DG and RM were consistent over the study. Compared with RM, DG had higher pH (8.2 ± 0.1 vs. 7.3 ± 0.3), total Kjeldahl N (3.7 ± 0.5 vs. $3.0 \pm 0.4 \text{ g L}^{-1}$), and TAN (2.0 ± 0.3 vs. $1.6 \pm 0.2 \text{ g L}^{-1}$), with lower total solids (5.8 ± 0.4 vs. $12.3 \pm 0.6\%$) and total carbon (C) (2.1 vs. 5.3%). The increased TAN is consistent with mineralization of organic N during digestion, whereas the added co-substrates contributed to higher total Kjeldahl N. Reduced total C is consistent with conversion of C to CO_2 and CH_4 during digestion.

Soil Mineral N Content

Although soil mineral N concentrations increased after N applications and tillage, a general decreasing trend was observed over the study at 0 to 15 cm depth (Table 2), and 15 to 30 cm soil mineral N followed the same decreasing trend (not shown). For example, mean soil NO_3^- -N concentrations collected ~ 30 d after the first fall and spring N applications were high for all treatments (especially DG and IS), but by the end of the experiment (≥ 1 yr after N application) the mean soil NO_3^- -N concentration had declined for all treatments to $\sim 6 \text{ kg NO}_3^-$ -N ha^{-1} (3.5 mg kg^{-1}). Spring-applied DG always had significantly higher soil NO_3^- -N at the start of the growing season compared with spring-applied RM and fall-applied DG or RM ($p < 0.01$ for both June 2012 and June 2013).

Environmental Conditions and Yield

It was much drier during Year 1 compared with Year 2 (Fig. 1A). Growing-season average air temperatures were similar (18°C in 2012 and 17°C in 2013), but growing-season precipitation was lower in 2012 than in 2013 (Table 3), leading to lower soil water-filled pore space in Year 1 compared with Year 2. Winter 2011–2012 had less snow than winter 2012–2013 (152 vs. 286 mm snow water equivalent, December–February).

As such, thawing occurred earlier in 2012 (March) than in 2013 and 2014 (April).

In the dry year, only 6% (23 mm) of the annual drainage occurred during the growing season, whereas in the wetter year, a significantly larger volume (81 mm; $p < 0.01$) and greater proportion of the annual drainage ($\geq 18\%$) occurred in the growing season (Table 3). Greater precipitation in Year 2 led to $\sim 10\%$ higher total drainage in Spring Treatment Year 2 compared with Spring Treatment Year 1 (Table 3), which was statistically significant using a paired t test ($p = 0.03$).

Biomass yields in 2012 were similar for RM and DG plots (average, $15,250 \pm 240 \text{ kg ha}^{-1}$). A larger yield range was apparent in 2013: DF and DS averaged $16,387 \text{ kg ha}^{-1}$, and RF was numerically higher than RS ($13,252$ vs. $11,319 \text{ kg ha}^{-1}$; not statistically different). In both years, average yields of RM or DG were numerically less than IS ($16,210 \text{ kg ha}^{-1}$ in 2012 and $17,900 \text{ kg ha}^{-1}$ in 2013). The control yielded $13,540 \text{ kg ha}^{-1}$ in 2012 and $12,990 \text{ kg ha}^{-1}$ in 2013.

Average yields of N harvested from RM and DG treatments were $143 \pm 8 \text{ kg N ha}^{-1}$ in 2012. In 2013, DG averaged $181 \pm 58 \text{ kg N ha}^{-1}$ and was significantly higher than RM ($122 \pm 47 \text{ kg N ha}^{-1}$; $p = 0.01$). The highest in both years was IS (166 kg N ha^{-1} in 2012 and 233 kg N ha^{-1} in 2013). The control had numerically the lowest N yield of all treatments in 2012 (120 kg N ha^{-1}) but not 2013 (164 kg N ha^{-1}). Most N yields exceeded the available N applied, which is consistent with the declining soil NO_3^- content (Table 2) and indicates that soil N mineralization was contributing to crop N demand.

N_2O Emissions

Daily N_2O fluxes from individual chambers were negative 12 times (mostly in control plots; minimum, $-4 \text{ g N}_2\text{O-N ha}^{-1} \text{ d}^{-1}$), and treatment average fluxes were negative six times ($< 0.9\%$ of all measurements). Individual chambers reached peaks over $500 \text{ g N}_2\text{O-N ha}^{-1} \text{ d}^{-1}$ 10 times, always during spring-time, whereas the aximum individual chamber flux was $1133 \text{ g N}_2\text{O-N ha}^{-1} \text{ d}^{-1}$ in an RF plot and maximum treatment-average flux was $552 \text{ g N}_2\text{O-N ha}^{-1} \text{ d}^{-1}$ (Fig. 1B). Peak growing season N_2O fluxes tended to coincide with precipitation and drainage episodes (Fig. 1). Annual N_2O emissions were higher for both RM and DG during the wetter year (Year 2) than the drier year (Year 1) (Fig. 2), and all treatments had much higher emissions

Table 2. Soil NO_3^- -N at 0–15 cm depth for each treatment on each sample date.

Date	Days since N application†		Digestate		Raw		Controls	
	Fall	Spring	Fall	Spring	Fall	Spring	IS‡	Unfertilized
	kg NO_3^- -N ha^{-1}							
1 Dec. 2011	34	–§	$153 \pm 17\parallel$	–	43 ± 29	–	–	22 ± 4
21 June 2012	237	29	$54 \pm 1a\#$	$156 \pm 14b$	$72 \pm 8a$	$60 \pm 14a$	179 ± 6	87 ± 20
12 Nov. 2012	13	173	$93 \pm 7a$	$41 \pm 21b$	$38 \pm 18a$	$32 \pm 8a$	68 ± 11	51 ± 24
20 June 2013	233	24	$28 \pm 0.1a$	$53 \pm 10b$	$26 \pm 5a$	$39 \pm 8b$	90 ± 31	20 ± 0.3
7 Nov. 2013	373	164	$12 \pm 3a$	$17 \pm 0.9b$	$8 \pm 1.3a$	$12 \pm 6a$	14 ± 7	15 ± 4
23 Apr. 2014	540	331	$6.1 \pm 0.2a$	$6.5 \pm 0.2b$	$6.6 \pm 0.1a$	$6.3 \pm 0.3a$	5.8 ± 0.5	5.0 ± 0.1

† Fall applications occurred in Oct. 2011 and Oct. 2012; spring applications occurred in May 2012 and May 2013.

‡ Inorganic fertilizer applied in spring.

§ No sample collected.

¶ Values are mean \pm SD.

Letters indicate significant differences ($p < 0.05$) between fall and spring application timing within each amendment type on each sample date.

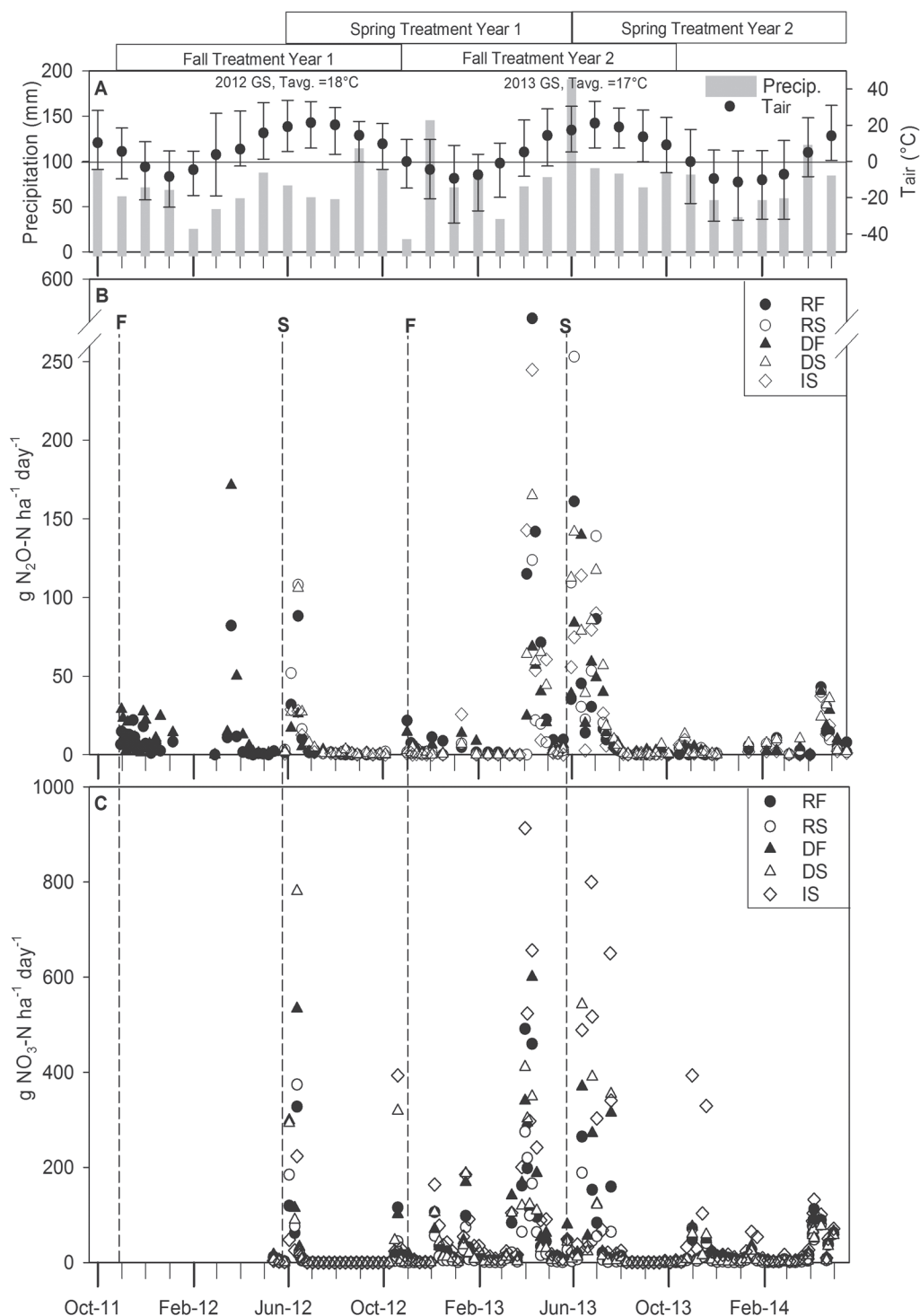


Fig. 1. (A) Monthly precipitation and mean air temperature (Tair) (whiskers show minimum and maximum). GS, Tavg., growing season average temperature. (B) Daily average N₂O-N fluxes for each N source treatment. (C) Nitrate-N fluxes for each N source treatment. Vertical dashed lines indicate fall (F) and spring (S) applications. DF, digestate applied in fall; DS, digestate applied in spring; IS, inorganic fertilizer (urea) applied in spring; RF, raw manure applied in fall; RS, raw manure applied in spring.

Table 3. Total precipitation and drainage (average and SD of all 12 plots) over each growing season (GS), non-growing season (NGS), and treatment year.

Treatment year	NGS period	Precipitation			Drainage		
		GS	NGS	Total	GS	NGS	Total
mm							
Year 1 (fall)	19 Oct. 2011–20 May 2012	374	398	772	23 (11)	n.d.†	n.d.
Year 1 (spring)	19 Oct. 2012–20 May 2013	374	455	829	23a‡ (11)	381b (153)	404 (162)
Year 2 (fall)	19 Oct. 2012–20 May 2013	517	455	972	81a (36)	381b (153)	462 (188)
Year 2 (spring)	19 Oct. 2013–20 May 2014	517	504	1021	81a (36)	352b (151)	433 (186)

† No data.

‡ Letters indicate significant differences ($p < 0.05$) between GS and NGS for each treatment year.

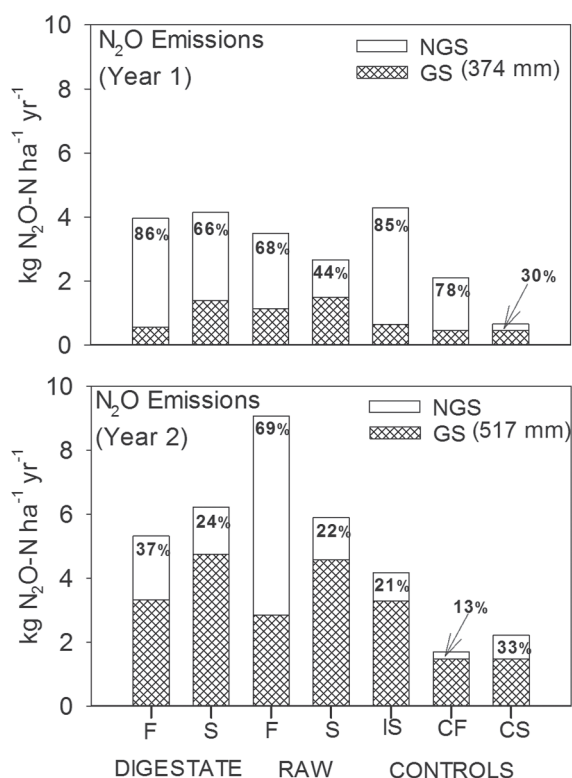


Fig. 2. Differences in N₂O emissions between years and the distribution of emissions between growing season (GS) and non-growing season (NGS) for each fall (F) and spring (S) application time for the N source treatments (digestate and raw) as well as the inorganic fertilizer reference (inorganic fertilizer applied in spring [IS]) and controls during the fall (CF) and spring (CS) treatment years. Percentage of annual N₂O–N emitted during the NGS is shown in each bar.

during the growing season of Year 2 compared with the growing season of Year 1. During the drier year, on the other hand, most emissions occurred outside the growing season (Fig. 2, top). Peak fluxes tended to occur during the winter and spring thaw (i.e., non-growing season) after fall applications and at planting and tillage (i.e., during the growing season) after spring applications (Fig. 1B). Indeed, spring applications (DS, RS) had significantly more emissions during the growing season than fall applications (DF, RF), whereas fall applications had significantly more emissions outside the growing season than spring applications ($p = 0.045$ and 0.039 , respectively) (Fig. 2).

Despite differences in timing of main N₂O events, mean annual N₂O emissions were not significantly different between spring versus fall application times (Table 4), and there was no significant interaction of application timing \times N source ($p = 0.2241$). Averaged over the 2 yr, there was no significant effect of application timing on average annual N₂O–N emissions scaled by area, N yield, or total N applied (Table 4). Considering individual years, there were higher N₂O emissions per kilogram of total applied N from the fall compared with spring applications in the wet year (Year 2), but this difference did not occur in the dry year (Year 1) (Table 4).

There was no significant difference in average annual N₂O emissions based on area between N source treatments, although all were significantly higher than the control (Table 5). There was a significant interaction of N source \times year ($p = 0.0325$) and significantly higher N₂O–N emissions in Year 2 compared with Year 1 ($p = 0.0002$). Specifically, in Year 1 only DS and IS had significantly higher emissions than the control ($p = 0.0428$ and 0.0338 , respectively), whereas in Year 2 DG and RM applied in both fall and spring (DF, DS, RF, RS) were significantly higher (Table 5). When scaled by N yield, only RF, DS, and RS treatments had significantly higher N₂O–N emissions than the control over the 2 yr (Table 5). Consistent with the area-scaled emissions, RF had the highest emissions in Year 2 (Table 5).

When scaled by total applied N, there were no significant N-source differences in 2-yr average annual N₂O–N emissions (Table 5), but there was a significant interaction of treatment \times year ($p = 0.0015$). Scaled by total N applied, IS was significantly higher than the other treatments in Year 1, and RF was significantly higher than the other treatments in Year 2. Emission factors were, on average, 1.1, 1.2, 1.3, 1.9, and 2.1% of total N applied for RS, DF, DS, IS, and RF, respectively. The range of emission factors in individual years (Table 5) was similar to ranges reported by Chantigny et al. (2013) of 3.0 to 5.5% for inorganic fertilizer and 0.9 to 1.1% for organic amendments. The emission factors were generally higher than the 1% default IPCC factor: on average, emission factors were 1.2% in Treatment Year 1 and 1.8% in Treatment Year 2 (similar to the 1.7% proposed for Eastern Canada by Rochette et al. [2008]). A much lower EF would have been derived in our study if emissions outside the growing season had not been measured because non-growing season emissions accounted for up to 86% of annual emissions in

Table 4. Effect of application timing (spring or fall) on N₂O emissions, averaged over digested (DG) and raw manure (RM) with different scaling for each treatment year and on average.

Scaling of emissions	Treatment year	Application timing (average of DG and RM)	
		Spring	Fall
Area (kg N ₂ O–N ha ⁻¹ yr ⁻¹)	1	3.40a† (1.12)‡	3.12a (1.69)
	2	6.06a (2.22)	7.20a (2.96)
	average	4.73a (2.19)	5.46a (2.94)
N-yield (kg N ₂ O–N kg ⁻¹ N uptake)	1	0.019a (0.006)	0.011a (0.011)
	2	0.029a (0.014)	0.036a (0.023)
	average	0.024a (0.011)	0.024a (0.022)
Total N\$ (kg N ₂ O–N kg ⁻¹ of total N applied)	1	0.010a (0.004)	0.008a (0.008)
	2	0.014b (0.008)	0.025a (0.015)
	average	0.012a (0.007)	0.016a (0.014)

† Significant differences ($p < 0.05$) in annual (i.e., treatment year) emissions are indicated by different letters in each row.

‡ Values in parentheses are SD.

\$ Emissions from the control were subtracted.

Table 5. Effect of N source on N₂O emissions with different scaling for both treatment years and on average. N sources were digestate applied in fall (DF), digestate applied in spring (DS), raw manure applied in fall (RF), raw manure applied in spring (RS), inorganic fertilizer applied in spring (IS), and control.

Scaling of emissions	Treatment year	N source treatments					
		DF	RF	DS	RS	IS	Control†
Area (kg N ₂ O–N ha ^{−1} yr ^{−1})	1	3.957ab (2.328)‡	3.485ab (1.031)	4.14a (0.886)	2.657ab (0.834)	4.281a (1.719)	1.373b (0.325)
	2	5.327b (1.885)	9.071a (2.753)	6.218b (2.636)	5.894b (2.126)	4.175cb (1.614)	1.963c (1.119)
	avg.	4.642a (2.093)	6.278a (3.553)	5.179a (2.133)	4.276a (2.287)	4.228a (1.545)	1.668b (0.826)
N-yield (kg N ₂ O–N kg ^{−1} N uptake)	1	0.013ab (0.013)	0.010ab (0.012)	0.023a (0.005)	0.015ab (0.006)	0.020ab (0.008)	0.003b (0.005)
	2	0.018bc (0.010)	0.055a (0.013)	0.025b (0.013)	0.033b (0.015)	0.005c (0.006)	0.008c (0.010)
	avg.	0.015bc (0.008)	0.033a (0.027)	0.024ab (0.009)	0.024ab (0.014)	0.015bc (0.010)	0.005c (0.008)
Total N applied§ (kg N ₂ O–N kg ^{−1} of total N applied)	1	0.009b (0.011)	0.006b (0.004)	0.012b (0.003)	0.007b (0.003)	0.026a (0.012)	N/A¶
	2	0.015b (0.008)	0.035a (0.013)	0.015b (0.010)	0.014b (0.008)	0.012b (0.010)	N/A
	avg.	0.012a (0.009)	0.021a (0.018)	0.013a (0.007)	0.011a (0.007)	0.019a (0.013)	N/A

† Values are the average N₂O emissions from control plots during fall and spring treatment years.

‡ Significant differences ($p < 0.05$) are indicated by different letters in each row.

§ Total N₂O–N emissions from the control were subtracted from each treatment before scaling.

¶ Not applicable (no N was applied).

the dry year and up to 69% in the wet year (Fig. 2). For spring-applied plots, post-growing season emissions occurred 6 mo after the initial manure application. This emphasizes the importance of year-round measurements of N losses.

NO₃ Leaching Losses

Losses of NO₃ from DS were consistently higher than RS ($p = 0.046$) (Table 6). Higher loss from both spring- and fall-applied DG compared with RM is likely associated with the lower C/N ratio of DG and better soil infiltration because of the much lower DM content in DG (Misselbrook et al., 2005).

In contrast, Svoboda et al. (2013) found no difference in NO₃ leaching between animal slurry and DG. However, the DM content was similar between their animal slurry and biogas residues (only 1.7% higher DM content for their cattle slurry), whereas there was a much larger difference between DG and RM in our study (5.8 vs. 12.3%, on average).

Spring-applied DG and RM had substantially less NO₃–N leached annually compared with the reference IS treatment (Table 6). This is potentially due to less C applied with the inorganic fertilizer to immobilize N, as was the case with organic amendments (Kramer et al., 2006). Other studies have also found

Table 6. Treatment effect on total annual NO₃–N leached, fraction of total N applied that was leached, and the total indirect N₂O emissions from the total leached N for all treatments (mean of two plots per treatment) during Spring Treatment Year 1 and Spring and Fall Treatment Year 2.

Treatment year	Treatment†	Total NO ₃ –N leached	Non-growing season		Frac _{Leach} ‡	Indirect N ₂ O emissions§
		kg NO ₃ –N ha ^{−1} yr ^{−1}	———— % —————			kg N ₂ O–N ha ^{−1} yr ^{−1}
1 (spring)	DS	9.49 ± 0.4	79		2.1	0.071
	RS	5.23 ± 1.2	79		0.7	0.039
	IS	16.82 ± 2.2	96		9.6	0.126
	CS¶	3.37 ± 0.3	98		N/A	0.025
2 (fall)	DF	14.72 ± 1.5	63		4.4	0.110
	RF	11.63 ± 0.3	69		3.5	0.087
	CF††	4.26 ± 0.1	77		N/A#	0.032
2 spring	DS	8.11 ± 1.2	30		1.9	0.066
	RS	4.41 ± 0.1	51		0.5	0.036
	IS	16.96 ± 3.2	48		9.7	0.127
	CS	3.01 ± 0.2	68		N/A	0.024
2	fall	8.92 ± 2.0a‡‡	66		4.0	0.099
1	spring	3.99 ± 2.6b	79		1.4	0.055
2	fall	8.92 ± 2.0a	66		4.0	0.099
2	spring	3.19 ± 2.2b	41		1.2	0.051

† DF, digestate applied in fall; DS, digestate applied in spring; IS, inorganic fertilizer applied in spring; RF, raw manure applied in fall; RS, raw manure applied in spring.

‡ Fraction of N applied that leached, calculated after subtracting the total NO₃–N mass load of the control.

§ Indirect emissions are calculated using the IPCC emission factor for leaching and runoff (EF5). It was assumed for this experiment that there was a minimal amount of runoff, and thus total NO₃–N leached would be the main contributor to indirect N₂O emissions.

¶ Total NO₃–N leached during a spring treatment year.

Not applicable (no N was applied).

†† Total NO₃–N leached during fall Treatment Year 2.

‡‡ Letters indicate significant differences ($p < 0.05$) between fall and spring applications of organic amendments (digested and raw manure combined).

higher $\text{NO}_3\text{-N}$ concentrations from fertilizer compared with manure or digestate (Svoboda et al., 2013; van Es et al., 2006). In Year 1, DS and RS had 44 and 69% less $\text{NO}_3\text{-N}$ leached compared with IS, respectively (Table 6). In Year 2, DS and RS had 52 and 74% less $\text{NO}_3\text{-N}$ leached compared with IS, respectively.

At least 50% more $\text{NO}_3\text{-N}$ leached from fall compared with spring applications of DG and RM ($p < 0.01$) (Table 6). Interestingly, the amount leached during the growing season was similar for both application times, but 6 to 7 kg ha^{-1} more $\text{NO}_3\text{-N}$ leached outside the growing season from fall compared with spring applications (Table 6). Thus, it was the non-growing season leaching losses that resulted in significantly higher $\text{NO}_3\text{-N}$ leached from fall compared with spring applications ($p = 0.032$). When total N losses ($\text{N}_2\text{O-N}$ and $\text{NO}_3\text{-N}$) were calculated for each N source treatment, fall-applied treatments had 6 to 10 kg more N loss than spring-applied treatments (Fig. 3, top panel), mainly due to higher $\text{NO}_3\text{-N}$ leached outside the growing season of fall versus spring applications. Greater leaching from fall applications outside the growing season is consistent with asynchrony between N application and crop N demand (months later) combined with reduced evapotranspiration and significantly larger leaching volumes in the non-growing season compared with the growing season ($p < 0.01$) (Table 3). van Es et al. (2006) also observed higher N concentrations in 0.9-m-deep tile drains from fall compared with spring applications, which they attributed to more N being leached during the period of low crop uptake.

Despite different weather conditions between years, total $\text{NO}_3\text{-N}$ losses after spring application were similar between Years 1 and 2 (Table 6). There was, however, a major difference in the proportion of $\text{NO}_3\text{-N}$ leached outside the growing season. During the dry year, 79% of total $\text{NO}_3\text{-N}$ leached outside the growing season for both DG and RM treatments. In contrast, during the wetter year, only 30% (DG) and 51% (RM) leached outside the growing season (Table 6).

Overall N Losses and Indirect Emissions

An important finding of this study is that although there were N source (DG vs. RM) effects on NO_3 leaching, both DG and RM had similar total annual N losses when $\text{N}_2\text{O-N}$ and $\text{NO}_3\text{-N}$ losses were combined (Fig. 3). In general, the greater $\text{NO}_3\text{-N}$ leached by DG compared with RM was offset by greater $\text{N}_2\text{O-N}$ emissions from RM compared with DG in treatment Year 2.

Indirect N_2O emissions from leached NO_3 made a small contribution to total N_2O emissions (Table 6; Fig. 3, lower panel). Using the current IPCC EF_5 (0.75%), the contribution ranged from 1.6 to 3.0% of total $\text{N}_2\text{O-N}$ emissions, which is in line with the 1.8% reported by Vilain et al. (2012). If the upper limit of the IPCC uncertainty range was used (i.e., 2.5%), indirect emissions would be more important, with the maximum contribution exceeding 9% in the IS treatment. The measured $\text{Frac}_{\text{LEACH}}$ in our study (0.5–9.7) (Table 6) was much lower than the IPCC value (30%) for all of the N sources applied.

Conclusions

Weather variations between years interacted with N source to affect N_2O emissions: during the wetter year, RF had significantly higher emissions than DF and DS. Although application timing significantly altered the time of year when N_2O

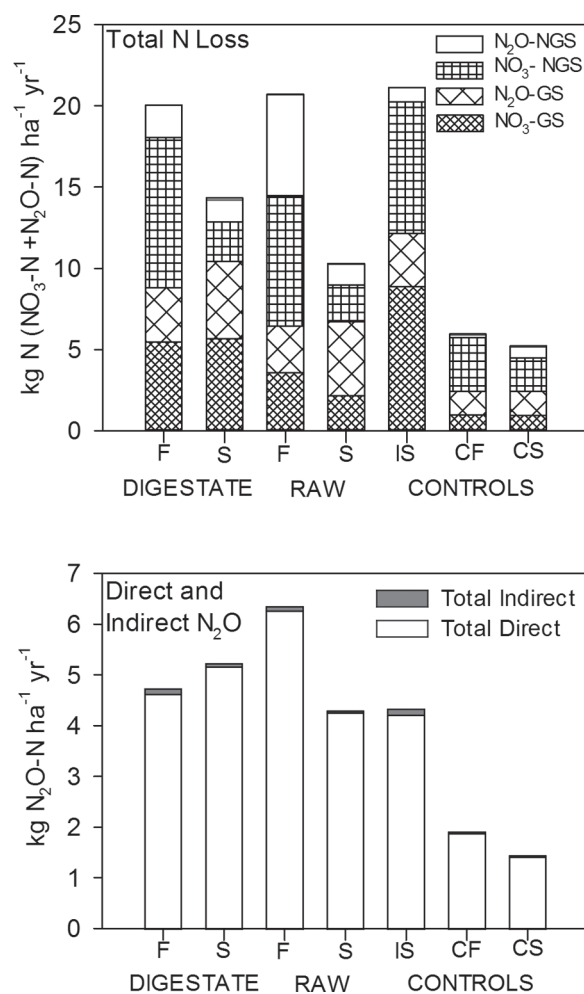


Fig. 3. Total N loss ($\text{N}_2\text{O-N} + \text{NO}_3\text{-N}$) (top) and total direct and indirect N_2O emissions (bottom). Total N loss included Treatment Year 2 data. Direct and indirect N_2O emissions are the average of both treatment years for spring-applied treatments. CF and CS, unfertilized control in fall and spring treatment year, respectively; F, fall application; GS, growing season; IS, inorganic fertilizer applied in spring; NGS, non-growing season; S, spring application.

emissions occurred—highlighting the need to measure N losses year-round—annual N_2O emissions were not significantly affected by application timing. However, fall applications caused significantly higher NO_3 losses due to greater NO_3 leaching after fall applications. Spring application of raw or digested dairy manure on clay soil resulted in less total N loss ($\text{N}_2\text{O-N} + \text{NO}_3\text{-N}$) and hence is recommended for these conditions.

Nitrate leaching was consistently greater from DG than RM; however, N_2O emissions were greater from RM than DG. Overall environmental N losses ($\text{N}_2\text{O-N} + \text{NO}_3\text{-N}$) from DG were similar to RM. For the conditions of our study, soil emissions induced by application of DG do not present an adverse trade-off to the environmental benefits incurred during biogas production.

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