Nitrous Oxide Emitted from Soil Receiving Anaerobically Digested Solid Cattle Manure

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Abstract
Limited information is available about soil nitrous oxide (N₂O) fluxes, N₂O emission factors (EFs), and yield-scaled N₂O emissions for biogas residues used to fertilize crops in semiarid regions. To address this knowledge gap, a 4-yr field experiment was conducted in a semiarid climate to determine growing season N₂O fluxes from soil receiving (i) anaerobically digested solid beef cattle manure (digestate), (ii) separated solids from the digestate (separated solids), and (iii) undigested solid beef cattle manure (cattle manure) applied to target one and two times the recommended rates (200 and 400 kg total N ha⁻¹) for barley (Hordeum vulgare L.) forage, assuming 50% of N was annually plant available. Nitrous oxide fluxes were determined using vented static chambers. Over the four growing seasons, 95, 80, and 81% of the N₂O flux occurred within 36 d of applying digestate, separated solids, and cattle manure, respectively. The cumulative N₂O emissions with digestate were 4.7 and 4.1 times the values of the separated solids and cattle manure, respectively. The digestate N₂O EF was 13.6 and 10.6 times the values of the separated solids and cattle manure, respectively, but the N₂O EF based on applied mineral N was similar for all amendments. The yield-scaled N₂O emissions with digestate were 4.3 and 3.6 times the values of the separated solids and cattle manure, respectively. In the semiarid region of southern Alberta, liquid biogas residues have a higher risk for N₂O emissions than both the separated solid fraction of the biogas residues and undigested cattle manure.

Core Ideas
• Information on N₂O emitted from biogas residues applied to semiarid soils is limited.
• 80 to 95% of N₂O emissions occurred within 36 d of amendment application over 4 yr.
• Digestate led to 4.4 times the N₂O emissions of separated solids and cattle manure.
• Digestate had 10.6 to 13.6 times the N₂O emission factors of separated solids and cattle manure.
• Digestate had 4.0 times the yield-scaled N₂O of separated solids and cattle manure.

Globally, there is limited information about how biogas residues influence nitrous oxide (N₂O) emissions after they are applied to soil (Charles et al., 2017) and even less information for rainfed semiarid areas (Meijide et al., 2009; Aguilera et al., 2013). In Canada, most research on N₂O emissions from agricultural soils amended with biogas residues has been conducted in eastern Canada (Chantigny et al., 2007; Schwager et al., 2016; Cambraeri et al., 2017). Little or no data are available for the much drier semiarid climates of western Canada. This is an important knowledge gap that should be filled because microbial-mediated processes may be restricted by soil moisture in semiarid regions (Helgason et al., 2014), and thus distinct N₂O emission factors (EFs) for organic amendments may be needed. Ultimately, enhancing our understanding of the N₂O emitted when organic amendments are used to fertilize crops is important to develop specific soil N₂O EFs (Tier 2 and Tier 3 methodologies) for semiarid farmland. This is especially important as signatory countries to the United Nations Framework Convention on Climate Change aim to define regional EFs for calculating N₂O emissions from agricultural soils (Charles et al., 2017).

Organic amendments are an important N₂O source in Canada, representing about 34% of direct soil N₂O emissions (Rochette et al., 2008). A global meta-analysis of organic amendments indicated that animal slurries, wastewater, biosolids, and biogas residues are in the high risk group, with a mean N₂O EF of 1.21 ± 0.14% (Charles et al., 2017). Most studies that have investigated biogas residues derived from manure used anaerobically digested liquid manures (slurries) with or without co-digested feedstocks and showed that the biogas residues decreased or led to similar N₂O emissions compared with the undigested residues when applied using the same method (Petersen, 1999; Wulf et al., 2002; Amon et al., 2006; Vallejo et al., 2006; Chantigny et al., 2007; Schwager et al., 2016; Holly et al., 2017). Other work showed that digested liquid cattle manure led to greater N₂O emissions than the undigested form when both were directly injected (Möller and Stinner, 2009). These contrasting responses reflect environmental, amendment, and edaphic properties interacting with crops to alter N₂O fluxes (Rochette et al., 2004; Gregorich et al., 2015). Unlike synthetic N fertilizer, these multiple interacting forces make it difficult to estimate the N₂O emission or EF based on the total N applied (Kim and Dale, 2008).

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Abbreviations: EC, electrical conductivity; EF, emission factor.
During the digestion of solid manure in our study, water, including feedlot runoff and recirculated digestate, was added to create a material with approximately 12% solids before digestion. As the resulting digestate was 95% liquid, fractionation into liquid and solid forms can be used to more efficiently apply these co-products as biofertilizers (Chantigny et al., 2007; Fangueiro et al., 2014; Hao et al., 2016). For the liquid digestate, direct injection is the best management practice with respect to placement, whereas surface broadcasting with immediate incorporation is recommended to retain the most N for the separated solids and cattle manure (Webb et al., 2013). The separated solid fraction may be used for crop production in a similar way as solid manure, whereas the liquid fraction represents an ammonium (NH₄–N)-rich soil amendment (Hao et al., 2016; Thomas et al., 2017c). Ultimately, the physical and chemical differences between the separated solid and liquid digestate fractions and the different best management practices related to placement may lead to distinct N₂O fluxes that require quantification.

Utilizing various methods to assess N₂O emissions is also warranted; yield-scaled N₂O EFs, for example, can help to define the agronomic and environmental impact of a fertilizer source (Van Groenigen et al., 2010; Venterea et al., 2011; Johnson et al., 2012; Gregorich et al., 2015). Yield-scaled EFs help to more clearly quantify the agronomic and environmental performance of a N source by calculating the N₂O emitted per unit of yield rather than the N₂O emitted based on the total N applied (Venterea et al., 2011; Pelster et al., 2012). For amendments with a high NH₄–N/total N ratio, such as anaerobically digested solid cattle manure (Hao et al., 2016; Thomas et al., 2017c) or liquid-swine and dairy cattle manure (Zebarth et al., 1996; Thomas et al., 2015), estimating the EF per unit of applied mineral N is also warranted (Aguilera et al., 2013).

To help address the global and national knowledge gap with respect to N₂O emissions from agricultural soils amended with biogas residues in semiarid climates, we determined soil N₂O warranting; yield-scaled N₂O EFs, for example, can help to define a high NH₄–N/total N ratio, such as anaerobically digested solid beef cattle manure (Knoop et al., 2011; Keeney and Nelson 1982); the NO₃–N plus NO₂-N concentration in the extract was determined by automated colorimetry (Auto-Analyzer III, Bran + Luebbe), as was the NH₄–N concentration (Easychem Pro, Systea Analytical Technology). Finely ground samples were used to determine organic C and total N concentrations by dry combustion (CARLO ERBA). Inorganic C was removed before dry combustion by treating samples with 6 mol L⁻¹ HCl. The total P concentration was determined by digesting finely ground samples with 18 mol L⁻¹ H₂SO₄ (Parkinson and Allen, 1975), and the P concentration in the digested solution was determined by colorimetry with a discrete analyzer (EasyChem Pro, Systea Analytical Technology).

The experimental site was previously described as part of a companion study investigating the agronomic benefits of using co-products of anaerobically digested solid beef cattle manure (Hao et al., 2016). Briefly, this experiment used three types of organic amendments applied at 200 and 400 kg total N ha⁻¹, the recommended agronomic rate to meet 100% of crop N needs and twice the recommended rate, respectively (Alberta Agriculture and Forestry, 2000). The rates were calculated assuming that 50% of the total N was plant available in the year of application, as N availability coefficients for co-products of anaerobically digested cattle manure were not available for this region when the study was conducted. The actual amendment application rates are provided in Supplemental Table S1. The amendment x rate treatment combinations were randomized in plots within four complete blocks. Each plot was 15 by 2.5 m with 2-m buffers between them. The three organic amendments used in this experiment were (i) anaerobically digested solid beef cattle manure (digestate), (ii) separated solids from the anaerobically digested solid beef cattle manure (separated solids), and (iii) undigested solid beef cattle manure (cattle manure) applied at one or two times the local recommended rate. Given the high mineral N and water content in the digestate, we hypothesized that it would emit more N₂O than would undigested solid cattle manure and the separated solids. Our rationale was that the higher NH₄–N and water content in digestate compared with that in undigested cattle manure and separated solids should favor N₂O production directly by nitrification and indirectly via denitrification.

### Materials and Methods

The field experiment was conducted from 2008 to 2011 near Lethbridge (49°38′00″ N; 112°48′00″ W; altitude: 929 m), AB, Canada, under semiarid climatic conditions. Weather data (Table 1) were downloaded from the nearby weather station (~7 km north of the experimental plots). The 30-yr (1981–2010) mean annual and growing season air temperatures were 6.2 and 16.2°C (Table 1) respectively, and the 30-yr mean annual and growing season precipitation were 396 and 206 mm, respectively. The 30-yr mean annual and growing season pan evaporation were 1503 and 957 mm, respectively.

### Experimental Design and Field Experiment Setup

The soil is a Dark Brown Chernozem (Typic Haploboroll). Soil samples (0–5, 5–15, 15–30, 30–60, 60–90 cm) were collected in fall 2007 prior to the first amendment application to determine baseline soil properties (Table 2). The soil NH₄–N and NO₃–N were extracted using 2 mol L⁻¹ KCl (1:5 soil-to-extract ratio; Keeney and Nelson 1982); the NO₃–N plus NO₂-N concentration in the extract was determined by automated colorimetry (Auto-Analyzer III, Bran + Luebbe), as was the NH₄–N concentration (Easychem Pro, Systea Analytical Technology). Finely ground samples were used to determine organic C and total N concentrations by dry combustion (CARLO ERBA). Inorganic C was removed before dry combustion by treating samples with 6 mol L⁻¹ HCl. The total P concentration was determined by digesting finely ground samples with 18 mol L⁻¹ H₂SO₄ (Parkinson and Allen, 1975), and the P concentration in the digested solution was determined by colorimetry with a discrete analyzer (EasyChem Pro, Systea Analytical Technology).

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The anaerobically digested solid beef cattle manure co-products were produced from manure of a 36,000 head beef cattle feedlot. The solid manure was loaded into a central dump wet hopper where it was mixed with water at a 1:2:1 water-to-manure ratio (co-feedstocks were not added) to reduce the total solids in the feedstock from approximately 30 to 12%. The water added was primarily feedlot run-off and recirculated digestate. The slurry was then dumped into two 1800-m³ insulated concrete digesters (15 m diam., 11.2 m height). The digestion occurred at 55°C with a 14-d retention time, whereby 5% new manure was added each day and 5% digestate was removed each day. A screw press was used to separate the solids from the liquids. The liquid digestate was pumped into a storage lagoon, while the separated solids were stockpiled. The digestate was stored in the lagoon for less than 1 yr.
Amendments were applied annually on 17 June 2008, 4 June 2009, 28 June 2010, and 7 July 2011. The digestate was directly injected (about 15 cm depth) using a custom plot-size applicator. In 2008, the separated solids and cattle manure were surface applied and manually incorporated with hand rakes to a soil depth of about 2 cm. In 2009, the separated solids and cattle manure were surface applied, but no method of incorporation was used because of a miscommunication. In 2010 and 2011, the separated solids and cattle manure were surface applied and incorporated with an offset disc (about 2 to 10 cm depth). The incorporation methods were selected as representative of best management practices aimed at minimizing N losses (Webb et al., 2013; Cambareri et al., 2017). Nevertheless, differences in how the separated solids and cattle manure were applied compared with the digestate likely contributed to the year-to-year variability observed for these treatments. Two-row barley (*Hordeum vulgare* L.) ‘AC Metcalf’ (88.5 kg seed ha\(^{-1}\)) was grown from 2008 to 2010, and six-row barley ‘Chigwell’ (98.4 kg seed ha\(^{-1}\)) was grown in 2011. No irrigation water was applied except in 2011. Irrigation was applied on 16 Sept. 2011. 

### Nitrous Oxide Flux Determination

The vented static chamber technique (Chang et al., 1998), including soil collars with detachable lids (Hutchinson and Mosier, 1981), was used to measure N\(_2\)O fluxes. Soil collars were inserted 5 cm into the soil surface (internal volume of 6.83 L with 683.5-cm\(^2\) surface area), fitted with Tygon O rings and a lid that was clamped to the collars at sampling time. Gas samples were drawn from the head space with polypropylene syringes (10 mL, Becton Dickinson & Co.) at 0, 10, 20, 30, and 60 min and injected into the pre-evacuated Exetainers (Labco). A weekly to biweekly gas sampling schedule was maintained for 12 to 18 wk each growing season. The N\(_2\)O concentrations were determined with a gas chromatograph equipped with an electron capture detector (CP3800, Varian Canada Inc.). The injector and column temperatures were kept at 55°C. The carrier was P10 gas (10% CH\(_4\), balance argon). The channel was main-

**Table 1. Growing season weather conditions.**

<table>
<thead>
<tr>
<th>Year</th>
<th>Seeding Date</th>
<th>Harvest Date</th>
<th>Temperature</th>
<th>Precipitation</th>
<th>Pan evaporation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Annual (^\circ)C</td>
<td>Seeding to harvest</td>
<td>Annual mm</td>
</tr>
<tr>
<td>2008</td>
<td>18 June</td>
<td>16 Sept.</td>
<td>6.2</td>
<td>17.0</td>
<td>522</td>
</tr>
<tr>
<td>2009</td>
<td>5 June</td>
<td>24 Aug.</td>
<td>5.8</td>
<td>16.5</td>
<td>417</td>
</tr>
<tr>
<td>2010</td>
<td>5 July</td>
<td>19 Oct.</td>
<td>6.3</td>
<td>15.0</td>
<td>607</td>
</tr>
<tr>
<td>2011</td>
<td>7 July</td>
<td>29 Sept.</td>
<td>6.1</td>
<td>17.8</td>
<td>537</td>
</tr>
<tr>
<td>30-yr mean</td>
<td>6.2</td>
<td>16.2‡</td>
<td>396</td>
<td>206‡</td>
<td>1503</td>
</tr>
</tbody>
</table>

† The 30-yr annual and seeding to harvest (June–August) mean values are from 1981 to 2010.

**Table 2. Initial soil properties† (mean values ± SE, n = 11).**

<table>
<thead>
<tr>
<th>Depth (cm)</th>
<th>pH</th>
<th>EC† (dS m(^{-1}))</th>
<th>Organic C (g kg(^{-1}))</th>
<th>Total N (g kg(^{-1}))</th>
<th>Total P (mg kg(^{-1}))</th>
<th>NH(_4)–N (mg kg(^{-1}))</th>
<th>NO(_3)–N (mg kg(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0–5</td>
<td>6.9 ± 0.1</td>
<td>0.32 ± 0.04</td>
<td>26.0 ± 0.5</td>
<td>2.46 ± 0.04</td>
<td>0.56 ± 0.02</td>
<td>11 ± 1</td>
<td>32 ± 1</td>
</tr>
<tr>
<td>5–15</td>
<td>6.7 ± 0.1</td>
<td>0.20 ± 0.03</td>
<td>18.7 ± 0.7</td>
<td>1.92 ± 0.06</td>
<td>0.49 ± 0.01</td>
<td>8 ± 1</td>
<td>21 ± 2</td>
</tr>
<tr>
<td>15–30</td>
<td>7.6 ± 0.1</td>
<td>0.62 ± 0.16</td>
<td>13.0 ± 0.4</td>
<td>1.41 ± 0.03</td>
<td>0.47 ± 0.01</td>
<td>5 ± 0</td>
<td>20 ± 3</td>
</tr>
<tr>
<td>30–60</td>
<td>8.0 ± 0.1</td>
<td>1.41 ± 0.35</td>
<td>8.3 ± 0.3</td>
<td>0.81 ± 0.04</td>
<td>0.48 ± 0.01</td>
<td>5 ± 0</td>
<td>20 ± 1</td>
</tr>
<tr>
<td>60–90</td>
<td>8.2 ± 0.0</td>
<td>1.69 ± 0.34</td>
<td>5.0 ± 0.3</td>
<td>0.47 ± 0.02</td>
<td>0.42 ± 0.01</td>
<td>8 ± 1</td>
<td>18 ± 1</td>
</tr>
</tbody>
</table>

† Dry matter basis, adapted from Hao et al. (2016).
‡ EC, electrical conductivity.

For amendment pH and EC determination, approximately 25 g of fresh solid amendment was mixed with 100 mL of deionized water, and 125 mL of digestate was used without dilution (Table 3). After the mixture was shaken for 1 h, pH was determined using a pH meter (Orion Model 125). The slurry mixture was then filtered with Fisher Q2 filter paper (1–5 μm; Thermo Fisher Scientific) and EC was measured. The extracting solution was then syringe-filtered (<0.45 μm) for water-extractable NH\(_4\)–N and NO\(_3\)–N determination by ion chromatography ( Dionex ICS-1000/DX-600, Dionex Corporation). Amendment total C and N concentrations were determined using methods similar to the soil, except for total C because inorganic C was not removed with 6 mol L\(^{-1}\) HCl. Barley forage was harvested at the soft dough stage when suitable for making silage feed (Zadoks growth scale = 85, Zadoks et al., 1974) and was oven-dried at 60°C for yield determination.
N2O EF (%) was calculated using the approach of Bouwman (2005). Gas flux was calculated as the first-order derivative of the concentration versus time and fitted to quadratic equations (SAS Institute, 2005). The UNIVARIATE procedure was used to calculate the coefficient of variation (0.018) were calculated. The quadratic equations (Chang et al., 1998) and expressed in grams N2O-N emitted per unit of applied mineral N (NH4–N + NO3–N) was calculated (Aguilera et al., 2013).

\[
EF_{\text{MinN}} = \frac{(N_{2}\text{O-N}}_{\text{fertilized}} - N_{2}\text{O-N}_{\text{unfertilized}})}{\text{Mineral N}_{\text{applied}}} \times 100
\]

where Mineral N_{\text{applied}} is the total amount of mineral N (NH4–N + NO3–N) applied to the fertilized plot (Aguilera et al., 2013).

For each replicated amended plot each growing season, the barley forage yield-scaled emission (kg N2O-N Mg\textsuperscript{-1} barley forage) was calculated per Gregorich et al. (2015):

\[
N_{2}\text{O}_{\text{yield-scaled}} = \frac{N_{2}\text{O}_{\text{fertilized}}}{Yield}
\]

where \(N_{2}\text{O}_{\text{yield-scaled}}\) is the cumulative annual N2O emission per unit of barley forage dry matter yield (kg N Mg\textsuperscript{-1} barley forage yield), \(N_{2}\text{O}_{\text{fertilized}}\) is the area-based annual cumulative N2O emission (kg N2O-N ha\textsuperscript{-1}), and Yield is the area-based barley forage yield (Mg barley forage ha\textsuperscript{-1}).

Over the duration of the study, the digestate supplied water at 44,282 to 79,015 L ha\textsuperscript{-1}, the separated solids supplied 17,564 to 32,930 L ha\textsuperscript{-1}, and the cattle manure supplied 9637 to 12,905 L ha\textsuperscript{-1}, all for the 1× rate. The water applied by the 2× rate was double these values. Because the digestate is approximately 95% water, the effect of a water addition in 2010 was assessed by applying irrigation water at rate similar to the 2× digestate treatment (i.e., 94,849 L ha\textsuperscript{-1}) to an additional unamended plot (located 2 m away from the experimental plots) in each block (\(n = 4\)).

### Statistical Analyses

Statistical analyses were computed with SAS software (SAS Institute, 2005). The UNIVARIATE procedure was used to
visually inspect the residuals for normality and potential outliers. To meet the assumption of normality, the N\textsubscript{2}O EF and yield-scaled N\textsubscript{2}O emissions were log-transformed before conducting the ANOVAs. Each ANOVA was conducted with the MIXED procedure as a repeated measures 3 × 2 augmented factorial with a control (Marini, 2003) to assess the significance of amendment type and N application rate and their interactions on annual cumulative N\textsubscript{2}O emissions, the N\textsubscript{2}O EFs (EF and EF\textsubscript{MinN}), and yield-scaled EFs. Amendment type, N application rate and year, and their two- and three-way interactions were set as fixed effects, and block was a random effect. Year was set as a repeated measure. Means were compared with Fisher’s protected least square means test at $P < 0.05$. To assess the nonlinear relationship (exponential rise to a maximum function) between the mineral N (NH\textsubscript{4}\textsuperscript{+}–N plus NO\textsubscript{3}\textsuperscript{-}–N) applied by the amendments and the cumulative growing season N\textsubscript{2}O emissions, we used SigmaPlot Version 13 (Systat Software, 2014) to compute the test statistics. One influential observation of the 24 means was flagged and removed based on a standardized residual of 3.08.

Results

Flux Patterns over the Four Growing Seasons

Typically over the four growing seasons, the N\textsubscript{2}O fluxes sharply increased 7 d after amendment application and peaked between 14 and 21 d after amendment application (Fig. 1). The N\textsubscript{2}O fluxes remained elevated until about 36 d after amendment application, especially for digestate, before returning to near background levels. After 20 d, the N\textsubscript{2}O fluxes had a tendency to decrease with time. In each growing season, the magnitude of the N\textsubscript{2}O fluxes from the digestate-amended soil was greater than that from the soil receiving cattle manure or separated solids. The greatest mean daily flux over the four growing seasons was 238 g N\textsubscript{2}O-N ha\textsuperscript{-1}, which occurred 15 d after the 2× digestate application in 2010. This event was preceded by 83 mm of rainfall over a 2-d period that ended 11 d before the amendment application and 27 d before the peak flux was measured. In general, after about the first 36 d, N\textsubscript{2}O fluxes did not appear to respond significantly to precipitation events or increased soil moisture, regardless of amendment type (Fig. 1; Supplemental Fig. S1 and S2).

Cumulative Nitrous Oxide Emissions, Emission Factors, and Yield-Scaled Emissions

The cumulative N\textsubscript{2}O emissions were significantly affected by amendment type, year, and the amendment type × year interaction (Table 4; Fig. 2). Digestate led to 4.7 and 4.1 times the cumulative growing season N\textsubscript{2}O emissions of the separated solids and cattle manure, respectively. There was no significant difference between separated solids and cattle manure.

The N\textsubscript{2}O EF was significantly affected by amendment type and year (Table 4). Digestate led to 13.6 and 10.6 times the N\textsubscript{2}O EF of separated solids and cattle manure, respectively. There was no significant difference between separated solids and cattle manure.

The N\textsubscript{2}O EF\textsubscript{MinN} was significantly affected by year and by an N application rate × year interaction (Table 4). The interaction showed that the 2× N application rate significantly increased the N\textsubscript{2}O EF\textsubscript{MinN} only in 2011, while in 2008 the 1× N application rate was significantly greater (Fig. 3).

Fig. 1. Daily soil nitrous oxide fluxes in response to anaerobically digested solid beef cattle manure (digestate), separated solids of the digestate (separated solids), and undigested solid beef cattle manure (cattle manure) applied annually for barley near Lethbridge, AB, Canada at target rates of 200 and 400 kg total N ha\textsuperscript{-1} (1× and 2× the recommended rate).

The yield-scaled N\textsubscript{2}O emission was significantly affected by amendment type, rate, year, and an amendment type × year interaction (Table 4; Fig. 2). Digestate led to 4.3 and 3.6 times the yield-scaled N\textsubscript{2}O emission of separated solids and cattle manure, respectively. There was no significant difference between separated solids and cattle manure.

Amendment Properties and Nitrous Oxide Emissions

The addition of water increased the N\textsubscript{2}O flux compared with the unamended control soil during the first sampling event,
about 7 d after application (Fig. 4), but the effect was short-lived. The N₂O emissions associated with the water treatment returned to background (unamended control) levels within 15 d, whereas those associated with the digestate remained well above background levels for about 35 d. A nonlinear exponential rise to a maximum function explained 70% of the variation between the mineral N applied by the organic amendments (NH₄-N plus NO₃-N) and cumulative N₂O emissions over the four growing seasons combined for 23 out of 24 mean observations (Fig. 5).

### Discussion

#### Nitrous Oxide Fluxes

In our study, the N₂O emitted within the first 36 d of amendment application represented the most significant emissions prior to fluxes returning to near background levels. Averaged over the four growing seasons, 95, 80, and 81% of the N₂O emissions occurred within 36 d of applying digestate, separated solids, and cattle manure, respectively, which is consistent with the mean cumulative N₂O emitted from the control soil was 0.5 ± 0.3 kg N ha⁻¹ over the 4-yr study period, while the control mean yield-scaled N₂O emission was 0.11 ± 0.12 kg N Mg⁻¹ yield (mean values ± SD). Values in a column within their respective amendment, rate, or year followed by different lowercase letters are significantly different according to a Fisher’s protected least square means comparison (P < 0.05). Means comparisons are only shown for main effects when an interaction involving the main effect was not significant.
work on digested swine slurry in a rainfed agroecosystem in a semiarid Mediterranean climate near Madrid, Spain (Meijide et al., 2009). This indicates that this is the critical time to measure N2O fluxes to uncover mechanisms driving the significant emissions for rainfed agroecosystems in semiarid regions.

Cumulative N2O Emissions and Emission Factors

Mean growing season N2O emissions ranged from about 0.7 kg N2O-N ha\(^{-1}\) for the undigested cattle manure and separated solids to about 3.3 kg N2O-N ha\(^{-1}\) for the digestate. Although non-growing season emissions were not measured in our study, non-growing season freeze–thaw cycles in cold temperate regions may represent 17 to 28% of annual N2O emissions (Wagner-Riddle et al., 2017). Thomas et al. (2017a, 2017b) found that the non-growing season N2O emissions in southern Alberta ranged from 0.1 to 0.2 kg N2O-N ha\(^{-1}\) when residual soil NO\(_3\)-N levels (0–15 cm) were <5 mg N kg\(^{-1}\) and from 0.3 to 0.4 kg N2O-N ha\(^{-1}\) when residual soil NO\(_3\)-N levels were between 5 and 25 mg N kg\(^{-1}\). In our study, residual soil NO\(_3\)-N levels (0–15 cm) were typically ≤10 mg N kg\(^{-1}\) (Hao et al., 2016), suggesting that non-growing season emissions may be reasonably estimated at 0.3 kg N2O-N ha\(^{-1}\). This would represent about 9 to 43% of the growing season emissions (based on mean amendment emissions) measured in the current study, or about 8 to 30% of estimated total annual N2O emissions.

Overall, digestate led to a much greater cumulative N2O emission and N2O EF than the separated solids and cattle manure. For example, the anaerobically digested solid cattle manure increased N2O emissions by 10.6 times those of the surface applied undigested cattle manure in our study. In contrast, anaerobically digested liquid swine manure reduced N2O emissions by about 50% compared with its undigested liquid form in a humid temperate region (Chantigny et al., 2007) and a drier Mediterranean region with about 430 mm of annual precipitation (Vallejo et al., 2006). Although no data were available to compare the N2O emitted from biogas residues in the semiarid regions of western Canada, the cumulative growing season N2O emissions from the cattle manure-amended soil (0.8 ± 0.4 kg N ha\(^{-1}\)) was within the range (0.2–2.8 kg N ha\(^{-1}\)) reported for the May to November period for soil receiving fall-applied cattle manure near Lethbridge, AB (Ellert and Janzen, 2008). This wide range indicates that N2O emissions are clearly driven most by the management practices and environmental conditions that modify the edaphic state in this semiarid region.

Averaged over the four growing seasons, digestate (10,122 kg ha\(^{-1}\)) led to significantly greater barley forage yield than cattle manure (8,045 kg ha\(^{-1}\)) and separated solids (8,151 kg ha\(^{-1}\)), which were significantly greater than the unamended control soil (6,504 kg ha\(^{-1}\); Hao et al., 2016). The yield-scaled N2O emissions were greater for the digestate than the separated solids and cattle manure, but there was a significant application × year interaction. This interaction was mainly driven by low rainfall that limited yields in 2011 and the high yields attained in 2009 when the precipitation events were distributed well without excessive rainfall before amendment application. Nevertheless, the data show that the higher yields attainable with applying digestate can at least partially offset the higher N2O emissions observed with this amendment, resulting in an overall reduction of the greenhouse gas intensity associated with digestate application.

In a meta-analysis of N2O emission from agricultural soils following the application of organic amendments, Charles et al. (2017) reported that the mean N2O EF for biogas residues was 0.92%, with a median of 0.49% based on data from northern Germany (Senbayram et al., 2014). Our values for the liquid emissions (Wagner-Riddle et al., 2017). Thomas et al. (2017a, 2017b) found that the non-growing season N2O emissions in southern Alberta ranged from 0.1 to 0.2 kg N2O-N ha\(^{-1}\) when residual soil NO\(_3\)-N levels (0–15 cm) were <5 mg N kg\(^{-1}\) and from 0.3 to 0.4 kg N2O-N ha\(^{-1}\) when residual soil NO\(_3\)-N levels were between 5 and 25 mg N kg\(^{-1}\). In our study, residual soil NO\(_3\)-N levels (0–15 cm) were typically ≤10 mg N kg\(^{-1}\) (Hao et al., 2016), suggesting that non-growing season emissions may be reasonably estimated at 0.3 kg N2O-N ha\(^{-1}\). This would represent about 9 to 43% of the growing season emissions (based on mean amendment emissions) measured in the current study, or about 8 to 30% of estimated total annual N2O emissions.

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95% of N\textsubscript{2}O was emitted during the first 36 d of amendment application each growing season, we believe this is a reasonably consistent with other growing seasons. This large flux appeared to result from a combination of two factors unique to 2010 that included the cattle manure N\textsubscript{2}O EF (0.09%) was substantially lower than the mean and median reported for biogas residues, and the cattle manure N\textsubscript{2}O EF (0.09%) was substantially lower than the weighted mean N\textsubscript{2}O EF for solid manure of 0.35% based on 11 studies (Charles et al., 2017). The separated solids and cattle manure shared similar N\textsubscript{2}O EFs, which is consistent with the proportion of their N recovered by barley (Hao et al., 2016; Thomas et al., 2017c). Ultimately, the data indicate that the solid fraction of biogas residues and undigested cattle manure emitted substantially less than what may be expected, highlighting the importance of developing region-specific N\textsubscript{2}O EFs for organic amendments in a vast geographic nation such as Canada. A principal assumption for calculating the N\textsubscript{2}O EF in this study was that the carryover of N from previous growing seasons had no effect on the N\textsubscript{2}O emitted the next growing season. As 80 to 95% of N\textsubscript{2}O was emitted during the first 36 d of amendment application each growing season, we believe this is a reasonably justifiable assumption.

The amendment × year interaction for cumulative N\textsubscript{2}O emissions and the yield-scaled N\textsubscript{2}O EF were strongly driven by a divergent interaction in 2010 whereby digestate led to a large N\textsubscript{2}O emission increase, while the other amendments remained relatively consistent with other growing seasons. This large flux appeared to result from a combination of two factors unique to 2010 that created better conditions for N\textsubscript{2}O emissions. First, in 2010, the digestate contained 38 mg NO\textsubscript{3}–N kg\textsuperscript{-1}, which was 2.5 to 5.4 times the NO\textsubscript{3}–N levels of 2009 and 2011, while in 2008 NO\textsubscript{3}–N was not detected in the digestate. Moreover, the NH\textsubscript{4}–N/total N ratios were similar in 2010 and 2011 (0.61 and 0.66, respectively), which suggests that the N\textsubscript{2}O emission potential may have been governed by the NO\textsubscript{3}–N concentration in the digestate prior to land application. Second, in 2010, two of the largest rainfall events (83 mm total) occurred over a 2-d period 11 d prior to amendment application. Based on estimated background water-filled pore space levels of 37 and 50% in the 5-cm and 20-cm soil layer, it is probable that the water added with the digestate, combined with the elevated water-filled pore space, enhanced the N\textsubscript{2}O flux in the first month after amendment application (Supplemental Fig. S1).

The greater N\textsubscript{2}O fluxes in 2010 could not be related to variability in the target rates because the N applied with digestate in 2010 was 65 and 38% of that applied in 2009 and 2011, respectively and similar to 2008 (Hao et al., 2016; Supplemental Table S1). Ultimately, the combination of 83 mm of rainfall, 11 d prior to amendment application, with the high NO\textsubscript{3}–N, NH\textsubscript{4}–N, and water contents in the digestate appeared to interact to contribute to the large burst of N\textsubscript{2}O in 2010. This illustrates the importance of measuring the mineral N composition prior to application and taking into consideration that the water content of the digestate may substantially enhance N\textsubscript{2}O emissions, depending on the moisture status of the soil.

Both the higher concentration and the greater solubility and potential diffusivity of mineral N in the digestate may increase the potential for N\textsubscript{2}O emissions relative to the cattle manure and separated solids. For instance, direct injection of digestate may create many NH\textsubscript{4}–N and NO\textsubscript{3}–N hotspots (Baral et al., 2017), whereas the substantially higher NH\textsubscript{4}–N/total N ratio of digestate (0.56) than cattle manure (0.08) and separated solids (0.04) would favor greater nitrification and denitrification to enhance N\textsubscript{2}O fluxes (Aguilera et al., 2013; Gregorich et al., 2015; Charles et al., 2017). The hotspots may also induce anaerobic respiration in microsites where O\textsubscript{2} becomes depleted with greater microbial activity (Parkin, 1987; Butterbach-Bahl et al., 2013).

Previous work with high N\textsubscript{2}O risk liquid manures suggested that the C status of the soil may play an important role in governing the magnitude of N\textsubscript{2}O fluxes (Vallejo et al., 2006; Chantigny et al., 2010; Pelster et al., 2012). This may help to explain the contrasting results across studies when organic amendments in the high N\textsubscript{2}O risk category, such as liquid manures and biogas residues, are applied to soil because the magnitude of the N\textsubscript{2}O emitted also likely depends on the C status of the soil. The presence of crop residue (organic C) decreased N\textsubscript{2}O emissions from soil fertilized with NH\textsubscript{4}NO\textsubscript{3} in southern Alberta (Hao et al., 2001) and over the nongrowing season in southern Ontario, Canada (Congreves et al., 2017). Thus, one way to potentially suppress the N\textsubscript{2}O emitted with digestate may be to inject it into a judicious supply of high C/N ratio decomposing cover crop residue before planting the cash crop. This could help to temporarily immobilize N while also encouraging complete denitrification to release N\textsubscript{2}O rather than the powerful trace gas N\textsubscript{2}O. More research is required to assess this potential mechanism and management practice.

**Effect of Water and Applied Mineral N on Nitrous Oxide Emissions**

Adding irrigation water at roughly the same volume as the water in the digestate in 2010 clearly showed that the effect of water was short-lived and had a strong effect only during the first week after application. Afterward, the water effect was no longer...
N₂O emissions, where 3 kg N₂O-N ha⁻¹ moisture availability may limit the magnitude of growing season to 0.12% for separated solids. Digestate led to much greater N₂O and 100 kg NH₄–N ha⁻¹ organic amendments applied to a barley crop between about 25 and 100 kg NH₄–N ha⁻¹. (Meijsde et al., 2009). This is in contrast to other studies in areas with humid temperate climates that showed N₂O emissions increased exponentially with mineral N contrast to other studies in areas with humid temperate climates that related with the NH₄–N content of digested pig slurry and other organic amendments applied to a barley crop between about 25 and 100 kg NH₄–N ha⁻¹. (Cardenas et al., 2010; Hoben et al., 2011). Overall, soil moisture availability may limit the magnitude of growing season N₂O emissions in response to increasing mineral N rates applied by organic amendments in rainfed agroecosystems in the semiarid region of southern Alberta and throughout semiarid and arid environments, globally.

Conclusion

Over the four growing seasons, 95, 80, and 81% of the N₂O flux occurred within 36 d of applying digestate, separated solids, and cattle manure, respectively. The N₂O EFs ranged from 0.44 to 1.93% for digestate, 0.05 to 0.12% for cattle manure, and 0.02 to 0.12% for separated solids. Digestate led to much greater N₂O emissions, owing to its high mineral N content prior to application, and thus poses greater environmental risks than undigested cattle manure and separated solids. Cattle manure and separated solids had similar N₂O emissions. An exponential rise to a maximum function explained 70% of the variation between the applied N₂O emissions. Biological limitation was reached at 3 kg N₂O-N ha⁻¹ per growing season between applied mineral N rates of 150 to 200 kg ha⁻¹. In a relatively dry semiarid Mediterranean climate, the cumulative N₂O emitted was strongly positively correlated with the NH₄–N content of digested pig slurry and other organic amendments applied to a barley crop between about 25 and 100 kg NH₄–N ha⁻¹ (Meijsde et al., 2009). This is in contrast to other studies in areas with humid temperate climates that showed N₂O emissions increased exponentially with mineral N contrast to other studies in areas with humid temperate climates that related with the NH₄–N content of digested pig slurry and other organic amendments applied to a barley crop between about 25 and 100 kg NH₄–N ha⁻¹. (Cardenas et al., 2010; Hoben et al., 2011). Overall, soil moisture availability may limit the magnitude of growing season N₂O emissions in response to increasing mineral N rates applied by organic amendments in rainfed agroecosystems in the semiarid region of southern Alberta and throughout semiarid and arid environments, globally.

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