

Article



# Impacts of Low Disturbance Liquid Dairy Manure Incorporation on Alfalfa Yield and Fluxes of Ammonia, Nitrous Oxide, and Methane

Jessica Sherman <sup>1</sup>, Eric Young <sup>1</sup>, <sup>\*</sup>, William Jokela <sup>1,†</sup> and Jason Cavadini <sup>2</sup>

- <sup>1</sup> USDA-ARS, Institute for Environmentally Integrated Dairy Management, 2615 Yellowstone Dr., Marshfield, WI 54449, USA; jessica.sherman@usda.gov (J.S.); jokela@wisc.edu (W.J.)
- <sup>2</sup> Marshfield Agricultural Research Station, University of Wisconsin, M605 Drake Ave., Stratford, WI 54484, USA; jason.cavadini@wisc.edu
- \* Correspondence: eric.young@usda.gov; Tel.: +1-715-384-9673
  - Retired.

+

**Abstract:** Surface applied liquid dairy manure application (i.e., broadcasting) after alfalfa (*Medicago sativa* L.) harvest is a common practice. Low disturbance manure incorporation (LDMI) may offer multiple benefits including lower ammonia (NH<sub>3</sub>), greenhouse gas (GHG) and hydrologic nutrient losses compared to broadcast. However, few studies have simultaneously quantified LDMI impacts on alfalfa yield, NH<sub>3</sub> and greenhouse gas (GHG) fluxes. We measured NH<sub>3</sub>, nitrous oxide (N<sub>2</sub>O), and methane (CH<sub>4</sub>) fluxes for liquid dairy manure treatments applied to alfalfa plots for broadcast and LDMI over three seasons (2014 to 2016) in central Wisconsin, USA. There were minor differences in alfalfa yield and nitrogen (N) uptake across treatments and years. Shallow disk injection and aerator/band reduced NH<sub>3</sub> loss by 95 and 52% of broadcast, respectively, however both substantially increased N<sub>2</sub>O fluxes (6 and 4.5 kg ha<sup>-1</sup> year<sup>-1</sup> versus 3.6 kg ha<sup>-1</sup> year<sup>-1</sup> for broadcast, respectively). The magnitude and timing of N<sub>2</sub>O fluxes were related to manure application and precipitation events. Average CH<sub>4</sub> fluxes were similar among methods and increased with soil moisture after manure application. Results highlight the importance of quantitatively evaluating agri-environmental tradeoffs of LDMI versus broadcast manure application for dairy farms.

**Keywords:** ammonia; carbon; dairy systems; greenhouse gases; liquid manure; methane; nitrogen; nitrous oxide

# 1. Introduction

Dairy manure is an important crop nutrient source, however careful management is needed to optimize nutrient use efficiency and minimize atmospheric and hydrologic losses (overland flow, leaching) associated with land application of manure. Cold climate dairies generate manure year-round but can have limited time windows and fields for application due to the short growing season and other cropping system limitations. Targeting manure applications to hay forages including alfalfa (*Medicago sativa*) in addition to annual crops like corn and grains provides additional land for manure application, recycles a portion of on-farm manure nutrients and creates multiple application windows after each harvest [1–3].

Since there is some risk of stand damage depending on how manure is applied and specific site characteristics (forage regrowth stage, soil moisture/compaction potential), there is considerable uncertainty around the benefits and challenges of applying manure to alfalfa in general. At low application rates and when applied before any regrowth, few negative yield impacts have been noted [1–3]. Another concern with applying manure on hay forage crops is forage quality/palatability, however Coblentz et al. [4] found no deleterious effects of applying liquid dairy manure on forage nutritive value. In addition, several studies indicate manure application to stands with optimum soil fertility are



**Citation:** Sherman, J.; Young, E.; Jokela, W.; Cavadini, J. Impacts of Low Disturbance Liquid Dairy Manure Incorporation on Alfalfa Yield and Fluxes of Ammonia, Nitrous Oxide, and Methane. *Agriculture* **2021**, *11*, 750. https:// doi.org/10.3390/agriculture11080750

Academic Editor: Mumtaz Cheema

Received: 10 July 2021 Accepted: 3 August 2021 Published: 6 August 2021

**Publisher's Note:** MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



**Copyright:** © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). unlikely to increase dry matter yield [2,5,6], however studies have reported yield increases for mixed alfalfa-grass/small grains receiving manure applications [7–9].

Liquid dairy manure in hay forage systems is commonly broadcast applied after harvest, leaving carbon (C), nitrogen (N), and phosphorus (P) species more prone to loss [10]. Manure ammonia (NH<sub>3</sub>) is much more vulnerable to atmospheric loss (volatilization) loss when broadcast on the soil surface as compared to incorporating/injecting via tillage or low disturbance manure incorporation (LDMI) methods [11–13]. Ammonia is also considered an indirect source of the secondary aerosol PM2.5 and nitrous oxide (N<sub>2</sub>O) [14] and can be transported and redeposited in nearby waterways [15] contributing to stream N inputs along with runoff sources [16,17]. While previous research suggests fertilizer and manure N inputs can contribute to both increased N<sub>2</sub>O and methane (CH<sub>4</sub>) fluxes, effects on CH<sub>4</sub> are more variable [18–20]. Ammonia emissions can be reduced by banding or injecting manure, however coulters and other injection/incorporation equipment can damage roots and shoots reducing yield potential [9,21-23]. Both application methods can reduce NH<sub>3</sub> losses by reducing the surface area of exposed manure and placing it below the canopy protecting bands from wind and solar irradiation while promoting infiltration [24]. Shallow disk injection can reduce NH<sub>3</sub> flux by 50 to 90% of broadcast depending on width and volume of slots. Banding has been somewhat less effective (39-78% lower emissions) and dependent on the thickness and width of manure application bands [7,19,25–27].

Previous studies in perennial forage systems have indicated that N<sub>2</sub>O fluxes tend to peak from one to two weeks after application, decreasing thereafter [26–28]. The amount of total N applied lost as N<sub>2</sub>O can be quite variable depending on site-specific conditions and weather. In a review of the factors affecting agroecosystem N<sub>2</sub>O fluxes, Bouwman [29] reported a range of 0–8% loss of applied N as N<sub>2</sub>O. Changes in soil moisture can have significant effects on N<sub>2</sub>O flux rates and cumulative losses [20,30,31]. With respect to manure application methods, research suggests that N<sub>2</sub>O fluxes tend to be greater with injection versus banding or broadcast due to greater N conservation from lower NH<sub>3</sub> volatilization losses and the creation of favorable conditions for denitrification within injection slots.

Liquid dairy manure is characterized by low redox potentials and generally contains high concentrations of hydrogen sulfide and CH<sub>4</sub>, both of which only form under low redox potential (Eh < 200 mV at pH 7.0) [32]. Similar to N<sub>2</sub>O, post-manure application is also an important period for CH<sub>4</sub> fluxes at the soil-air interface. Elevated CH<sub>4</sub> emissions can occur during the application process and from soil microsites with sufficiently low redox potential, particularly where LDMI equipment has concentrated manure [18,23]. In the absence of direct CH<sub>4</sub> applications from liquid manures or very poorly drained soil conditions, soils are a net CH<sub>4</sub> sink, particularly for warmer, drier months with more rapid CH<sub>4</sub> oxidation rates [28,33]. Tillage has mixed overall effects on CH<sub>4</sub> fluxes related to its variable influence on soil physical properties, drainage, and thus redox potentials and CH<sub>4</sub> formation/oxidation. Few studies have focused on the impacts of cropping system factors and tillage regime on CH<sub>4</sub> fluxes.

Incorporating or injecting manure into perennial forages while maintaining yield and reducing GHG fluxes and nutrient runoff risk is an important goal of dairy farm sustainability [34]. Impacts of broadcasting liquid dairy manure versus LDMI on alfalfa forage yield, NH<sub>3</sub>, and GHG fluxes are not well understood. The objective of our study was to quantify the impacts of LDMI and broadcast liquid dairy manure application on alfalfa dry matter yield, N uptake, and fluxes of NH<sub>3</sub>-N, N<sub>2</sub>O-N, and CH<sub>4</sub> over three field seasons at a research farm in central Wisconsin.

## 2. Materials and Methods

## 2.1. Study Site

The study was conducted on a somewhat poorly drained Withee silt loam soil (fineloamy, mixed, superactive, frigid Aquic Glossudalfs; 1–3% slope) on the University of Wisconsin/USDA-ARS Marshfield Agricultural Research Station located in Marshfield, WI (from May 2014 to December 2016). The 10-year average (2006–2016) annual temperature and precipitation are 6.6 °C and 793 mm, respectively. The whole field was planted with alfalfa (*Medicago sativa*) (Nexgrow–6422Q) on 16 May 2013 at 19 kg ha<sup>-1</sup>. Fifteen plots (7.3 × 12.8 m) were arranged in a randomized complete block design (3 blocks/replication with 5 treatments) with untreated areas between individual plots to allow equipment maneuvering and routine field operations to the extent possible. Plots were oriented lengthwise with the field and travel direction, perpendicular to the slope.

#### 2.2. Treatment Details and Crop Management Practice

The five treatments in the study consisted of four manure application treatments and a no manure control that received triple superphosphate (0-46-0) and potash (0-0-60) at similar total P and K rates as the manure treatments. Both fertilizer and manure treatments were applied 7 August 2014, 30 June 2015 and 14 June 2016 after forage harvests; (second harvest in 2014, first harvest in 2015 and 2016). Manure was sampled in between treatment applications four times during each application period and tested for total N (TN), total P (TP), ammonium-N (NH<sub>4</sub>-N), K, and total solids content [35]. Manure application rate was approximately 74,800 L ha<sup>-1</sup> and much higher than desired in 2014 due to a malfunctioning flow meter; in 2015 and 2016 it was 46,750 L ha<sup>-1</sup>. Manure application contributed an average of 18 kg P, 100 kg K, 48 kg NH<sub>4</sub>-N, and 98 kg N ha<sup>-1</sup> for the study. Detail on individual manure application treatments follows (Figure S1):

- (1) Shallow Injection (Inject): 64 cm blades set at a 5 degree angle (Yetter Avenger, Yetter Manufacturing, Colchester, IL, USA), designed to cause minimal soil disturbance created 1.5–2 cm wide slits, manure was applied approximately 8–10 cm deep in these slits which were 30 cm apart.
- (2) Banded-aerator application (Aerator/Band): Manure was applied in bands about 5 cm wide through steel tubes 90-cm directly behind the tines of a rolling tine aerator (SAF Holland Aerway AWST). Aerator tines (no offset angle used), three per spindle, spaced 19 cm apart along the shaft, penetrated into the soil, creating slots approximately 2-cm × 20-cm at the soil surface narrowing down to a 2-cm wide point at the 18-cm depth. Tine slots were approximately 40 cm apart on center in the direction of travel. Manure slurry entered the slots for increased soil infiltration.
- (3) Banded application (Band): Manure was applied with the Aerator/Band applicator without the aeration tines, with hoses dragging across the soil surface. Manure bands were about 3–5 cm wide.
- (4) Broadcast application (Broadcast): Manure was broadcast with the Aerator/Band applicator raised approximately 40 cm above the soil surface so that manure provided complete coverage of the soil.

Harvest measurements were collected 3–4 times a season approximately every 28 days after the initial harvest in early or late June (24 June 2014, 25 June 2015, 9 June 2016) and weighed using a forage plot harvester/mower unit (F935, John Deere, Moline, IL, USA) equipped with digital load cells. Harvest passes were 1 m wide (10 cm cutting height) for each plot and harvest. Separate samples were hand-clipped from alfalfa immediately surrounding the harvest pass (cutting height = 10 cm), dried at 55 °C, and ground to pass a 1 mm sieve. These samples were then analyzed for N by high temperature combustion (Elementar VarioMax CN analyzer, Elementar Americas, Inc., Mt. Laurel, NJ, USA) and total minerals (P, Calcium (Ca), Magnesium (Mg)) after nitric acid digestion by inductively coupled plasma-optical emission spectrometer (ICP-OES) at the University of Wisconsin Soil and Forage Lab following standard procedures [36].

## 2.3. Ammonia and GHG Sampling and Analysis

Ammonia emission was measured in 2015 and 2016 using the dynamic chamber/equilibrium concentration technique a method that is well suited to small replicated plots and successfully used by others [27,37,38]. Two 31 by 38 by 20-cm ventilated chambers and an open ambient sampler were placed in each plot. Duplicate passive diffusion samplers of

two types were placed in each chamber and in each ambient sampler holder, one with an acidified filter paper disk directly exposed to the air and the other with the filter paper disk 10 mm below a semipermeable Teflon membrane, requiring NH<sub>3</sub> to diffuse along a 10-mm path to the trap. Ammonia flux was calculated based on the micrometeorological law of resistance (using NH<sub>3</sub> concentrations to estimate required parameters). More detail on the approach, chamber design and flux computations are provided elsewhere [37–40]. Measurements started immediately after manure application and continued for seven separate periods through the third day. Day 1 measurements started immediately (Time 0) with successive periods starting approximately 1, 3, and 8 h (overnight) after application, followed by two 5-h measurements during Day 2 and a 10-h period on Day 3 (no overnight).

adjusted for measured temperature and wind conditions [37,41]. Nitrous oxide and CH<sub>4</sub> were measured using the static, vented chamber technique following the GRACEnet protocol [42]. Chambers consisted of stainless steel bases (61 × 38.1 × 10.2 cm) installed centered over a manure band or injection slit where applicable, two per plot on the west side of each plot outside of plot harvester pass locations. Bases were inserted as deep as possible (3.1 cm average height above soil surface to account for surface topography) and were moved and replaced after each cutting and harvest at which time they were alternately placed approximately 0.5 or 1.5 m from plot edge avoiding previously disturbed areas. Insulated and vented (3 mm ID and 40 cm long tubing) stainless steel lids with a height of 15.2 cm were sealed on top of bases during measurement by clipping the tops to the bases, the tops had weather stripping attached along the lip to serve as a gasket. At times when alfalfa was too tall to fit under the lid a 23 cm tall stainless steel, insulated extension was used in addition to the lid. Chamber construction was based on a design from R. Venterea (http://www.ars.usda.gov/pandp/docs.htm?docid=19008 (accessed on 15 April 2013)).

Overnight emission between Day 2 and Day 3 was estimated from linear interpolation

Gas samples were collected by inserting a 10-mL syringe into the chamber top sampling port, removing a sample, and immediately transferring the sample to a 5.9-mL capped, non-evacuated vial containing ambient air. Sample concentrations were later adjusted for the dilution by ambient air. Gas samples were collected four times for each measurement (0, 15, 30, and 45 min) over a 2- to 3-h period, typically between 900 h and 1200 h to approximate the mean daily temperature. Gas fluxes were calculated from the rate of change in concentration over the sampling period using linear regression, adjusted for theoretical flux underestimation [43] resulting from chamber deployment. Measurement began approximately one month prior to manure application in 2014, continued until soil freezing and snowfall and resumed after snowmelt. Sampling was done approximately weekly (more frequently after manure or rain, less frequently later in the season) from manure application 2014 through November 2016. Gas samples were analyzed via gas chromatography using an electron capture detector (micro-ECD) for  $N_2O$ , a flame ionization detector (FID) for CH<sub>4</sub>, and an infrared gas analyzer (IRGA, LiCor 820, Lincoln, NE, USA) for CO<sub>2</sub> (Agilent 7890A GC System, Santa Clara, CA, USA). Annual cumulative gas fluxes were estimated by linear interpolation between sampling times.

Soil bulk density was measured (two 4.8 cm-diam.  $\times$  10 cm deep cores per plot) 3–4 times per year at the beginning of each sampling year and after harvest, manure application, or other activities that would be expected to affect bulk density. Bulk density was used in calculating theoretical flux underestimation [43] and adjusting N<sub>2</sub>O fluxes. Volumetric soil moisture (5-cm depth; Delta-T Devices Theta Probe) and soil temperature (5-cm depth; digital soil thermometer) were also measured in each plot during each gas sampling period.

Plots were arranged in a randomized complete block design with manure application method as the main treatment effect. The mixed modeling procedure (proc mixed) of the Statistical Analysis System (SAS) was used to the fixed effect of manure application method with block considered a random effect [44]. Differences in treatment means were performed using linear contrasts at  $p \le 0.10$ , given the high inherent variability associated

with field gas flux measurements. Dependent variables included alfalfa dry matter yield, N uptake, and cumulative  $NH_3$  and GHG fluxes. Dependent variables were tested (proc univariate) for normality and transformed ( $log_{10}$  or square root) to achieve normality and/or homogeneity of variance as needed. Data are presented as back transformed values to maintain consistency across all variables. Pearson correlation coefficients (proc corr) and linear regression analysis (proc reg) were also performed for select variables.

#### 3. Results and Discussion

# 3.1. Weather

The weather in 2014 was on average colder than the 10 year average (20%) (Table 1), particularly during winter months. Temperatures for 2015 and 2016 were closer to long-term averages and slightly warmer mainly from warmer winter months (wintertime mean temperature was approximately 14% greater than the long-term average for Marshfield, WI). Growing season temperatures were close to long-term averages each year and precipitation was also close to average for 2015, but 31% and 16% greater than the long-term average in 2014 and 2016, respectively. Much of the additional precipitation was in early spring for 2014, both June and September of 2016 had rainfall exceeding the long-term average.

Table 1. Average air temperature and total precipitation by month 2014–2016.

		Avera	nge Air Te	mperature <sup>1</sup>	Precipitation <sup>1</sup>			ation <sup>1</sup>
Month	2014	2015	2016	Average 2006–2016	2014	2015	2016	Average 2006–2016
			°C				mn	ı
January	-15	-8.9	-8.3	-9.0	34.8	13.4	16.5	23.4
February	-15	-13	-5.0	-8.5	38.1	4.20	16.0	18.6
March	-7.8	0.0	3.3	-0.3	20.8	10.2	101	37.1
April	4.4	7.8	6.1	6.5	132	91.2	34.0	70.2
May	13	14	14	14	122	80.5	50.3	95.1
June	19	18	19	19	118	103	172	106
July	19	21	21	21	88.6	46.5	88.1	92.7
August	19	19	21	20	179	65.0	95.8	95.9
September	14	18	18	15	73.2	170	181	87.7
Öctober	8.3	8.9	11	8.5	92.0	63.7	53.6	83.9
November	-3.9	4.4	5.0	0.6	58.4	58.7	42.9	31.6
December	-4.4	0.0	-7.2	-7.5	38.4	85.3	51.3	50.7
January–December <sup>1</sup>	4.4	7.4	8.1	6.6	995	791	903	793

<sup>1</sup> Values are averages for air temperature and totals for precipitation.

# 3.2. Manure Application Method Effects on Alfalfa Hay Crop Yield

In 2014 and 2016 manure application tended to increase alfalfa yields compared to the no manure control, however response was variable and not always significant (Table 2). Manure application also generally resulted in greater N removal in 2016, though this too was variable with no clear yield effect associated with manure treatments (Table 2). A few significant yield differences were noted before manure was applied in 2014 (Table 2) and after manure application in 2015. Inject had significantly lower yield than Broadcast, Band, or control. Compared to other studies, our results suggest relatively minor overall differences in alfalfa forage dry matter yield among all treatments. Some previous LDMI studies in alfalfa and grass hay crops indicate a possible yield reduction with shallow disk injection or banding, often attributed to root/crown or above ground plant damage [13,21–23,33]. Mean N removal by alfalfa far exceeded the amount of annual N applied (from manure) as reported by others [1]. Results suggest a relatively low overall risk of yield reductions from LDMI assuming application is done under appropriate soil conditions and soon after harvest prior to regrowth.

	1st	Cut	2nd	Cut	3rd	Cut	4th	Cut	To	tal
Treatment	DM Yield	N Uptake	DM Yield	N Uptake	DM Yield	N Uptake	DM Yield	N Uptake	DM Yield	N Uptake
					kg ł	na <sup>-1</sup>				
					20	14				
Control	6585	179	4715 c <sup>1</sup>	148	3177	112	_ 2	-	14,251 c	428 c
Broadcast	7007	181	5291 ab	161	3115	116	-	-	15,412 ab	458 b
Band	6871	192	5002 b	146	3147	118	-	-	15,021 b	456 b
Aerator/Band	6955	193	5513 a	170	3263	125	-	-	15,731 a	488 a
Shallow Inject	7042	186	5135 b	166	3303	116	-	-	15,480 ab	468 b
CV	6	9	4	9	5	6	-	-	2	3
<i>p</i> -value	NS	NS	0.01	NS	NS	NS	-	-	0.004	0.004
					20	15				
Control	6487	138	4402 a	157 a	2294	80.4	-	-	12,704	363
Broadcast	6578	157	4130 a	139 b	2239	80.6	-	-	12,947	376
Band	6409	160	4084 a	141 b	2121	71.9	-	-	12,614	373
Aerator/Band	6797	160	3938 ab	138 b	1857	66.2	-	-	12,592	364
Shallow Inject	6831	177	3657 b	133 b	2234	79.2	-	-	12,722	389
CV	7	14	5	1	25	24	-	-	6	8
<i>p</i> -value	NS	NS	0.06	0.03	NS	NS	-	-	NS	NS
					20	16				
Control	6470	175 b	4693	144	3328	108 c	2809	107	17,247	540
Broadcast	7438	214 a	4898	149	3553	114 bc	2773	102	18,662	578
Band	6598	179 b	5054	154	3879	132 a	2848	108	18,378	572
Aerator/Band	6590	188 b	4506	141	3600	115 b	2785	106	17,481	549
Shallow Inject	6741	188 b	4662	143	3608	120 b	2882	107	17,893	560
CV	9	7	6	6	7	5	5	6	4	4
<i>p</i> -value	NS	0.05	NS	NS	NS	0.005	NS	NS	NS	NS

**Table 2.** Alfalfa dry matter (DM) yield (kg ha<sup>-1</sup>) and nitrogen uptake (kg ha<sup>-1</sup>) by harvest and year.

<sup>1</sup> Manure application treatment means without a common letter differ at  $p \le 0.1$ ; <sup>2</sup> A fourth alfalfa hay harvest only occurred in 2016.

# 3.3. Manure Application Effects on Ammonia Fluxes

Mean NH<sub>3</sub>-N flux rates were similar in 2015 and 2016 with greater flux rates closer to the time of application (Figure 1), as previously demonstrated by other studies [7,11,12,27,33,45–47]. Broadcast application had substantially greater cumulative mean NH<sub>3</sub> fluxes in the first 3 days after application compared to other treatments, followed by Band, Aerator/Band and Inject with flux reductions of 30%, 52%, and 95% of Broadcast, respectively. Band and Aerator/Band impacts on NH<sub>3</sub> flux varied, decreasing NH<sub>3</sub> flux by an average of 18 and 24% of Broadcast in 2015 (not statistically significant) and 43 and 77% of Broadcast in 2016 (significantly lower for Aerator/Band), respectively (data not shown).



**Figure 1.** Average ammonia flux (**top**) and cumulative loss (**bottom**) for 2015 and 2016. Means without a common lower case letter differ at p < 0.10.

Lower NH<sub>3</sub> loss for Aerator/Band than broadcast or band has also been previously reported and is likely related to lower manure surface area contributing to lower NH<sub>3</sub>-N fluxes [22,25,27,48]. Wetter soil conditions in 2016 probably also contributed to deformation of aerator slots (more soil mass was stuck to aerator tines compared to drier conditions), which could have also contributed to more open slot surface area affecting NH<sub>3</sub> loss. Slightly warmer temperatures and higher wind speeds (Table 3) may have also increased Broadcast losses in 2016 since both can be significantly correlated with NH<sub>3</sub>-N losses [48,49]. Despite relatively high temporal and spatial variability, average NH<sub>3</sub> reductions in our study were similar to other trials [7,11,19,26,47,50,51].

Tracking N inputs from manure application permitted estimates of the fraction of applied manure NH<sub>4</sub>-N lost as NH<sub>3</sub>-N. During the 2016 season, approximately 100% of applied NH<sub>4</sub>-N and 50% of TN was lost from Broadcast plots; in 2015, 74 and 36% loss occurred. Similarly, other researchers have reported large N losses from manure application applied after hay crop harvest as NH<sub>3</sub>, ranging from 25 to 78% of applied NH<sub>4</sub>-N loss

depending primarily on method of application, weather and soil conditions [7,19,25–27,33]. Misselbrook [26] reported a 99% loss in June versus 58% with March application, further supporting the range of  $NH_3$  loss we observed in our trial. Similarly, our results show the importance of injecting manure to maximize  $NH_3$  retention in the form of  $NH_4^+$  but also indicate the importance of accounting for soil moisture and weather conditions (temperature, wind speed, amount/timing of precipitation) to help explain variation in the amount and timing of  $NH_3$  fluxes for individual experiments and among multiple sites or regions.

Period	Temperature	Wind Speed	Rain Total	
	°C	${ m m~s^{-1}}$	mm	
		2015		
day 1	18.5	2.6	0	
night 1	12.2	0.8	0	
day 2	18.0	1.3	0	
day 3	18.9	0.7	0	
		2016		
day 1	22.6	3.9	0	
night 1	17.9	1.9	6.9	
day 2	21.7	1.3	0	
day 3	18.6	3.5	0	

Table 3. Weather during ammonia flux sampling in 2015 and 2016.

#### 3.4. Manure Application Effects on Nitrous Oxide Fluxes

Mean N<sub>2</sub>O fluxes were larger after manure application, consistent with previous experiments [18,20,26,33,50,51]. In general, larger N<sub>2</sub>O fluxes were associated with Inject and Aerator/Band treatments, whereas the no manure control had the lowest N<sub>2</sub>O fluxes (Figures 2–4). Smaller N<sub>2</sub>O fluxes occurred outside the manure application times and were associated with precipitation and higher soil water contents. Mean cumulative N<sub>2</sub>O-N fluxes were relatively low prior to manure application and during the late summer (Figures 2–4). Larger increases in N<sub>2</sub>O-N flux occurred approximately 16 days after manure application, coincident with the largest observed differences in N<sub>2</sub>O fluxes among treatments (Figure 5). Given the low NH<sub>3</sub> emission and lack of significance at other times, rainfall events after manure application during the growing season appear to be important times for triggering elevated N<sub>2</sub>O fluxes.

Lower overall fluxes were associated with Broadcast and Band treatments, although Band and Broadcast did not differ significantly from Inject. Aerator/Band had the greatest mean cumulative N<sub>2</sub>O-N flux (mean = 6 kg ha<sup>-1</sup>), primarily from higher fluxes in 2014 and 2015 (though not significantly different from Inject). While the large flux range across years (2.0 to 9.0 kg ha<sup>-1</sup>, 3.2 to 6.6 kg ha<sup>-1</sup>, and 1.3 to 2.7 kg ha<sup>-1</sup> across treatment in 2014, 2015, and 2016, respectively) is undoubtedly related to soil and weather conditions, N input differences from manure probably also contributed, particularly the excessive rate in 2014.

Denitrification and NO<sub>3</sub><sup>-</sup> reduction to N<sub>2</sub>O and dinitrogen (N<sub>2</sub>) in soils is microbiologically mediated with reaction rates related to NO<sub>3</sub><sup>-</sup> concentrations, temperature, pH, redox and other physicochemical properties. While soil moisture variation is a known factor influencing N<sub>2</sub>O release, only weak correlations were noted between N<sub>2</sub>O fluxes and soil moisture (r = 0.05, p = 0.05) and temperature (r = 0.09, p = 0.0007) in our study. However, it is clear from other research that N<sub>2</sub>O formation can occur over a range of redox potentials (0 to 400 mV) and pH [52–56]. As previously mentioned, N uptake by alfalfa exceeded N applied annually and probably contributed residual NO<sub>3</sub>-N that was available for periodic microbial reduction to N<sub>2</sub>O.



Figure 2. Precipitation, soil temperature and moisture, and daily nitrous oxide (N<sub>2</sub>O-N) fluxes for 2014.



Figure 3. Precipitation, soil temperature and moisture, and daily nitrous oxide (N<sub>2</sub>O-N) fluxes for 2015.

50 45 Moisture (%

40

35

30 iture (°C) and

20

<u>۶</u> 25

Precipitation

- Temperature

Moisture





Figure 4. Precipitation, soil temperature and moisture, and daily nitrous oxide (N<sub>2</sub>O-N) fluxes for 2016.



Figure 5. Mean cumulative (N<sub>2</sub>O-N) fluxes by season and mean total cumulative fluxes for the study. Means without a common lower case letter within each time period differ at p < 0.10.

Cumulative N<sub>2</sub>O losses ranged from 1.1 to 12% of applied N with losses greater in 2014 and lower in 2016. In addition, mean cumulative N2O losses from manure treatments ranged from 22 to 100% greater than the no manure control for 2015 and 2016 and 50 to 360% greater than the control in 2014, these results are in line with the 975% greater emissions with injection found in the meta-analysis of Zhou et al. [56].

The cumulative quantity of N<sub>2</sub>O lost as a fraction of TN applied in our study is similar to Bouwman [29] where a range of 0 to 8% of applied TN was lost as N<sub>2</sub>O in a review of 180 experiments. Since the rate of manure application in the field to all plots was inadvertently doubled in 2014, this could be considered an outlier; ignoring 2014 data, the range of cumulative N<sub>2</sub>O losses narrows to 1.1 to 6.1% loss of TN applied.

# 3.5. Manure Application Effects on Methane Fluxes

Compared to N<sub>2</sub>O, average CH<sub>4</sub> fluxes generally peaked sooner after manure application if at all (Figure 6), with larger CH<sub>4</sub> fluxes in 2016 compared to 2014 and 2015. Mean CH<sub>4</sub> fluxes tended to be greater for Aerator/Band and Inject treatments, though not significant. Other studies have also indicated the overriding influence of soil and environmental factors on CH<sub>4</sub> emissions [50,57,58]. Greater losses post-manure application in 2016 could be due to wetter soil conditions in the injection zone that may have decreased soil redox potential. During warm, drier summer periods soils released minimal CH<sub>4</sub> and tended to act as a net sink for CH<sub>4</sub>, particularly in the dry period of the late summer-fall time period. Over the study, temperature and CH<sub>4</sub> fluxes were only weakly correlated (r = 0.14, p < 0.001). Soil moisture content was not correlated with CH<sub>4</sub> fluxes in 2015 (drier season), however they were significantly correlated in 2014 (r = -0.26, p < 0.001) and 2016 (r = -0.13, p = 0.003). Cumulative mean CH<sub>4</sub> fluxes averaged <800 g ha<sup>-1</sup> year<sup>-1</sup> with no significant application effects.



**Figure 6.** Mean methane (CH<sub>4</sub>) fluxes by manure application treatment for 2014 (**top**), 2015 (**center**), and 2016 (**bottom**).

#### 3.6. Carbon Dioxide Equivalents and Global Warming Potential

Due to the presence of perennial vegetation in the chambers, plant respiration probably contributed to a large portion of  $CO_2$  fluxes. The lack of yield differences between treatments is therefore reflected in the few significant differences for cumulative  $CO_2$  flux between treatments within years (data not shown). We did find Inject cumulative flux to be slightly yet significantly lower in 2015 than Broadcast and Band possibly related to significant yield differences after manure application although it remained similar to Aerator/Band and the control. Soil and plant/root disturbance may also have contributed to slightly lower CO<sub>2</sub> flux in other years with Inject although not significant. On average, across years, there were some significant differences of note, Aerator/Band had the highest cumulative flux (33,148 kg ha<sup>-1</sup> year<sup>-1</sup>) while Broadcast and Band had intermediate (32,622 and 32,043 kg ha<sup>-1</sup> year<sup>-1</sup>, respectively), and Inject and control had the lowest (30,244 and 31,269 kg ha<sup>-1</sup> year<sup>-1</sup>, respectively). Using CO2 equivalents [14] to calculate global warming potential (GWP) (where 265 and 28 are used for N2O and CH4, respectively, and 1% of NH3-N is considered converted to N2O), there were no differences in GWP among treatments for any year. Average GWP followed a similar pattern as CO<sub>2</sub> likely due to the dominance of  $CO_2$  emission compared to other gases and its large influence on the GWP calculation.

#### 4. Conclusions

Impacts of liquid dairy manure application method after alfalfa harvesting on NH<sub>3</sub>,  $N_2O$ , and  $CH_4$  fluxes using broadcast and LDMI methods were investigated for three field seasons in central Wisconsin on a somewhat poorly drained silt loam soil. Results indicated that application method had a relatively limited effect on dry matter yields. Cumulative NH<sub>3</sub> fluxes were much greater for Broadcast with intermediate losses for Aerator/Band and Band and lowest for the Inject system. Whereas NH<sub>3</sub> fluxes peaked immediately after manure application and approached a steady state after two days, N<sub>2</sub>O fluxes peaked approximately two weeks of application and were triggered by precipitation events. Aerator/Band and Inject had the largest cumulative N2O fluxes and were not different. Cumulative  $N_2O$  fluxes for Band and Broadcast were numerically lower on average than Aerator/Band and Inject. Methane fluxes were small in comparison to  $NH_3$  and  $N_2O$ and did not differ by application method. Results show Band mitigated both NH<sub>3</sub> and N<sub>2</sub>O fluxes with intermediate GWP. While Inject maximized NH<sub>3</sub> conservation a portion of this N was lost as N<sub>2</sub>O but also had lower CO<sub>2</sub> fluxes, reducing GWP; Aerator/Band had the greatest N<sub>2</sub>O flux and GWP. Banding and injection of manure to alfalfa stands after harvest for the silt loam soils of central Wisconsin appear to be viable options to increase N use efficiency and mitigate GHG emissions with little impact on overall yield potential. Our results also highlight the trade-offs between  $NH_3$  and  $N_2O$  loss vulnerabilities and a need to account for such management practices in farm nutrient budgeting and developing future nutrient management tools.

**Supplementary Materials:** The following are available online at https://www.mdpi.com/article/10 .3390/agriculture11080750/s1, Figure S1.

**Author Contributions:** Conceptualization, W.J. and J.S.; methodology, J.S. and W.J.; formal analysis, J.S. and E.Y.; investigation, W.J. and J.S.; resources, J.S., E.Y., W.J., and J.C.; data curation, J.S. and W.J.; writing—original draft preparation, J.S. and E.Y. writing—review and editing, E.Y., J.S., W.J. supervision, W.J., J.C. and E.Y.; project administration, W.J., J.S., J.C., and E.Y. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

**Data Availability Statement:** The data presented in this study are available on request from the corresponding author.

Acknowledgments: We thank Tony Sternweis, Ashley Braun, and Tia Haffenbredl for excellent technical assistance in the field and lab, and the UW MARS staff for equipment operation and field

maintenance. This material is based upon work that is supported by the National Institute of Food and Agriculture, U.S. Department of Agriculture, under award number 2013-68002-20525. Any opinions, findings, conclusions, or recommendations expressed in this publication are those of the author(s) and do not necessarily reflect the view of the U.S. Department of Agriculture.

Conflicts of Interest: The authors declare no conflict of interest.

# References

- 1. Dungan, R.S.; Leytem, A.B.; Tarkalson, D.D.; Ippolito, J.A.; Bjorneberg, D.L. Greenhouse Gas Emissions from an Irrigated Dairy Forage Rotation as Influenced by Fertilizer and Manure Applications. *Soil Sci. Soc. Am. J.* **2017**, *81*, 537–545. [CrossRef]
- Daliparthy, J.; Herbert, S.J.; Veneman, P.L.M. Dairy Manure Applications to Alfalfa: Crop Response, Soil Nitrate, and Nitrate in Soil Water. Agron. J. 1994, 86, 927–933. [CrossRef]
- Lamb, J.F.S.; Russelle, M.P.; Schmitt, M.A. Alfalfa and Reed Canarygrass Response to Midsummer Manure Application. Crop. Sci. 2005, 45, 2293–2300. [CrossRef]
- 4. Pote, D.H.; Way, T.R.; Sistani, K.R.; Moore, P.A., Jr. Water-quality effects of a mechanized subsurface-banding technique for applying poultry litter to perennial grassland. *J. Environ. Manag.* **2009**, *90*, 3534–3539. [CrossRef]
- 5. Coblentz, W.K.; Muck, R.E.; Borchardt, M.A.; Spencer, S.K.; Jokela, W.E.; Bertram, M.G.; Coffey, K.P. Effects of dairy slurry on silage fermentation characteristics and nutritive value of alfalfa. *J. Dairy Sci.* **2014**, *97*, 7197–7211. [CrossRef]
- Ketterings, Q.M.; Frenay, E.; Cherney, J.H.; Czymmek, K.J.; Klausner, S.D.; Chase, L.E.; Schukken, Y.H. Application of Manure to Established Stands of Alfalfa and Alfalfa-Grass. *Forage Grazinglands* 2007, 5, 1–11. [CrossRef]
- Lloveras, J.; Aran, M.; Villar, P.; Ballesta, A.; Arcaya, A.; Vilanova, X.; Munoz, F. Effect of swine slurry on alfalfa production and on tissue and soil nutrient concentration. *Agron. J.* 2004, *96*, 986–991. [CrossRef]
- Bittman, S.; Van Vliet, L.J.P.; Kowalenko, C.G.; McGinn, S.; Hunt, D.E.; Bounaix, F. Surface-Banding Liquid Manure over Aeration Slots: A New Low-Disturbance Method for Reducing Ammonia Emissions and Improving Yield of Perennial Grasses. *Agron. J.* 2005, 97, 1304–1313. [CrossRef]
- 9. Matsi, T.; Lithourgidis, A.S.; Gagianas, A.A. Effects of injected liquid cattle manure on growth and yield of winter wheat and soil characteristics. *Agron. J.* 2003, *95*, 592–596. [CrossRef]
- 10. Shah, S.B.; Miller, J.L.; Basden, T.J. Mechanical aeration and liquid dairy manure application impacts on grassland runoff water quality and yield. *Trans. ASAE* 2004, 47, 777–788. [CrossRef]
- 11. Sherman, J.F.; Young, E.O.; Coblentz, W.K.; Cavadini, J. Runoff water quality after low-disturbance manure application in an alfalfa-grass hay crop forage system. *J. Environ. Qual.* **2020**, *49*, 663–674. [CrossRef]
- Dell, C.J.; Kleinman, P.J.; Schmidt, J.P.; Beegle, D.B. Low-Disturbance Manure Incorporation Effects on Ammonia and Nitrate Loss. J. Environ. Qual. 2012, 41, 928–937. [CrossRef] [PubMed]
- 13. Duncan, E.W.; Dell, C.J.; Kleinman, P.J.A.; Beegle, D.B. Nitrous Oxide and Ammonia Emissions from Injected and Broadcast-Applied Dairy Slurry. J. Environ. Qual. 2017, 46, 36–44. [CrossRef] [PubMed]
- 14. Maguire, R.O.; Kleinman, P.J.A.; Dell, C.J.; Beegle, D.B.; Brandt, R.C.; McGrath, J.M.; Ketterings, Q.M. Manure Application Technology in Reduced Tillage and Forage Systems: A Review. *J. Environ. Qual.* **2011**, *40*, 292–301. [CrossRef] [PubMed]
- 15. IPCC. *Climate Change 2014: Mitigation of Climate Change;* Cambridge University Press: New York, NY, USA, 2014.
- 16. Apsimon, H.M.; Kruse, M.; Bell, J.N.B. Ammonia emissions and their role in acid deposition. *Atmos. Environ.* **1987**, *21*, 1939–1946. [CrossRef]
- 17. Smith, K.A.; Jackson, D.R.; Pepper, T.J. Nutrient losses by surface run-off following the application of organic manures to arable land. 1. Nitrogen. *Environ. Pollut.* **2001**, *112*, 41–51. [CrossRef]
- 18. Withers, P.J.A.; Clay, S.D.; Breeze, V.G. Phosphorus Transfer in Runoff Following Application of Fertilizer, Manure, and Sewage Sludge. J. Environ. Qual. 2001, 30, 180–188. [CrossRef]
- 19. Flessa, H.; Beese, F. Laboratory Estimates of Trace Gas Emissions following Surface Application and Injection of Cattle Slurry. *J. Environ. Qual.* **2000**, *29*, 262–268. [CrossRef]
- 20. Rodhe, L.; Etana, A. Performance of Slurry Injectors compared with Band Spreading on Three Swedish Soils with Ley. *Biosyst. Eng.* **2005**, *92*, 107–118. [CrossRef]
- 21. Perälä, P.; Kapuinen, P.; Esala, M.; Tyynelä, S.; Regina, K. Influence of slurry and mineral fertiliser application techniques on N2O and CH4 fluxes from a barley field in southern Finland. *Agric. Ecosyst. Environ.* **2006**, *117*, 71–78. [CrossRef]
- 22. Chen, Y.; Zhang, Q.; Petkau, D.S. Evaluation of different techniques for liquid manure application on grassland. *Appl. Eng. Agric.* **2001**, *17*, 489–496. [CrossRef]
- 23. Gordon, R.; Patterson, G.; Harz, T.; Rodd, V.; MacLeod, J. Soil aeration for dairy manure spreading on forage: Effects on ammonia volatilisation and yield. *Can. J. Soil Sci.* 2000, *80*, 319–326. [CrossRef]
- 24. Mattila, P.K.; Joki-Tokola, E.; Tanni, R. Effect of treatment and application technique of cattle slurry on its utilization by ley: II. Recovery of nitrogen and composition of herbage yield. *Nutr. Cycl. Agroecosyst.* **2003**, *65*, 231–242. [CrossRef]
- 25. Sommer, S.G.; Hutchings, N.J. Ammonia emission from field applied manure and its reduction—Invited paper. *Eur. J. Agron.* **2001**, *15*, 1–15. [CrossRef]
- 26. Mattila, P.K.; Joki-Tokola, E. Effect of treatment and application technique of cattle slurry on its utilization by ley: I. Slurry properties and ammonia volatilization. *Nutr. Cycl. Agroecosyst.* **2003**, *65*, 221–230. [CrossRef]

- 27. Misselbrook, T.H.; Laws, J.A.; Pain, B.F. Surface application and shallow injection of cattle slurry on grassland: Nitrogen losses, herbage yields and nitrogen recoveries. *Grass Forage Sci.* **1996**, *51*, 270–277. [CrossRef]
- 28. Rodhe, L.; Pell, M.; Yamulki, S. Nitrous oxide, methane, and ammonia emissions following slurry spreading on grassland. *Soil Use Manag.* **2006**, *22*, 229–237. [CrossRef]
- 29. Chadwick, D.R.; Pain, B.F.; Brookman, S.K.E. Nitrous Oxide and Methane Emissions following Application of Animal Manures to Grassland. J. Environ. Qual. 2000, 29, 277–287. [CrossRef]
- 30. Bouwman, A.F. Direct emission of nitrous oxide from agricultural soils. Nut. Cycl. Agroecosyst. 1996, 46, 53–70. [CrossRef]
- 31. Ball, B.C.; Scott, A.; Parker, J.P. Field N2O, CO2 and CH4 fluxes in relation to tillage, compaction and soil quality in Scotland. *Soil Tillage Res.* **1999**, *53*, 29–39. [CrossRef]
- 32. Gagnon, B.; Ziadi, N.; Rochette, P.; Chantigny, M.H.; Angers, D.A. Fertilizer Source Influenced Nitrous Oxide Emissions from a Clay Soil under Corn. *Soil Sci. Soc. Am. J.* 2011, 75, 595–604. [CrossRef]
- Pfluke, P.D.; Jokela, W.E.; Bosworth, S.C. Ammonia Volatilization from Surface-Banded and Broadcast Application of Liquid Dairy Manure on Grass Forage. J. Environ. Qual. 2011, 40, 374–382. [CrossRef]
- 34. Husson, O. Redox potential (Eh) and pH as drivers of soil/plant/microorganism systems: A transdisciplinary overview pointing to integrative opportunities for agronomy. *Plant Soil* **2013**, *362*, 389–417. [CrossRef]
- 35. Holly, M.A.; Kleinman, P.J.; Bryant, R.B.; Bjorneberg, D.L.; Rotz, C.A.; Baker, J.; Boggess, M.; Brauer, D.; Chintala, R.; Feyereisen, G.; et al. Short communication: Identifying challenges and opportunities for improved nutrient management through the USDA's Dairy Agroecosystem Working Group. *J. Dairy Sci.* **2018**, *101*, 6632–6641. [CrossRef]
- 36. Peters, J. Recommended Methods of Manure Analysis; University of Wisconsin-Extension: Madison, WI, USA, 2003.
- 37. Peters, J. Wisconsin Procedures for Soil Testing, Plant Analysis, and Feed and Forage Analysis. 2013. Available online: https://uwlab.soils.wisc.edu/about-us/lab-procedures-and-methods/ (accessed on 10 May 2014).
- 38. Svensson, L. A New Dynamic Chamber Technique for Measuring Ammonia Emissions from Land-Spread Manure and Fertilizers. *Acta Agric. Scand. Sect. B-Plant Soil Sci.* **1994**, 44, 35–46. [CrossRef]
- 39. Misselbrook, T.H.; Hansen, M.N. Field evaluation of the equilibrium concentration technique (JTI method) for measuring ammonia emission from land spread manure or fertiliser. *Atmos. Environ.* **2001**, *35*, 3761–3768. [CrossRef]
- 40. Myers, T.L.; Dell, C.J.; Beegle, D.B. Evaluation of ammonia emissions from manure incorporated with different soil aerator configurations. *J. Soil Water Conserv.* 2013, *68*, 306–314. [CrossRef]
- 41. Sherman, J.F.; Young, E.O.; Jokela, W.E.; Cavadini, J. Impacts of low-disturbance dairy manure incorporation on ammonia and greenhouse gas fluxes in a corn silage–winter rye cover crop system. *J. Environ. Qual.* **2021**, 1–11. [CrossRef]
- 42. Malgeryd, J. Technical measures to reduce ammonia losses after spreading of animal manure. *Nutr. Cycl. Agroecosyst.* **1998**, *51*, 51–57. [CrossRef]
- 43. Parkin, T.B.; Venterea, R.T. Chamber-based trace gas flux measurements. In *Sampling Protocols*; Follett, R.F., Ed.; USDA-ARS: Washington, DC, USA, 2010; Available online: www.ars.usda.gov/research/GRACEnet (accessed on 15 April 2013).
- 44. Venterea, R.T. Simplified Method for Quantifying Theoretical Underestimation of Chamber-Based Trace Gas Fluxes. *J. Environ. Qual.* **2010**, *39*, 126–135. [CrossRef] [PubMed]
- 45. SAS Institute Inc. SAS 9.4 Guide to Software Updates; SAS Institute Inc.: Cary, NC, USA, 2013.
- 46. Meisinger, J.J.; Jokela, W.E. Ammonia volatilization from dairy and poultry manure. In *Managing Nutrients and Pathogens from Animal Agriculture (NRAES-130)*; Natural Resource, Agriculture, and Engineering Service: Ithaca, NY, USA, 2000.
- 47. Wulf, S.; Maeting, M.; Clemens, J. Application Technique and Slurry Co-Fermentation Effects on Ammonia, Nitrous Oxide, and Methane Emissions after Spreading: II. Greenhouse gas emissions. *J. Environ. Qual.* **2002**, *31*, 1795–1801. [CrossRef]
- 48. Huijsmans, J.F.M.; Hol, J.M.G.; Vermeulen, G.D. Effect of application method, manure characteristics, weather and field conditions on ammonia volatilization from manure applied to arable land. *Atmos. Environ.* **2003**, *37*, 3669–3680. [CrossRef]
- 49. Hansen, M.N.; Sommer, S.G.; Madsen, N.P. Reduction of ammonia emission by shallow slurry injection: In-jection efficiency and additional energy demand. *J. Environ. Qual.* 2003, *32*, 1099–1104. [CrossRef]
- 50. Sommer, S.G.; Olesen, J.E.; Christensen, B.T. Effects of temperature, wind speed and air humidity on ammonia volatilization from surface applied cattle slurry. *J. Agric. Sci.* **1991**, *117*, 91–100. [CrossRef]
- Sistani, K.R.; Warren, J.G.; Lovanh, N.; Higgins, S.; Shearer, S. Greenhouse Gas Emissions from Swine Effluent Applied to Soil by Different Methods. Soil Sci. Soc. Am. J. 2010, 74, 429–435. [CrossRef]
- Venterea, R.T.; Maharjan, B.; Dolan, M.S. Fertilizer Source and Tillage Effects on Yield-Scaled Nitrous Oxide Emissions in a Corn Cropping System. J. Environ. Qual. 2011, 40, 1521–1531. [CrossRef] [PubMed]
- Letey, J.; Valoras, N.; Focht, D.D.; Ryden, J.C. Nitrous Oxide Production and Reduction during Denitrification as Affected by Redox Potential. Soil Sci. Soc. Am. J. 1981, 45, 727–730. [CrossRef]
- 54. Masscheleyn, P.H.; DeLaune, R.D.; Patrick, W.H., Jr. Methane and nitrous oxide emissions from laboratory measurements of rice soil suspension: Effect of soil oxidation-reduction status. *Chemosphere* **1993**, *26*, 251–260. [CrossRef]
- 55. Bouwman, A.F.; Boumans, L.J.M.; Batjes, N.H. Modeling global annual N2O and NO emissions from fertilized fields. *Glob. Biogeochem. Cycles* 2002, *16*, 28-1–28-9. [CrossRef]
- 56. Butterbach-Bahl, K.; Baggs, E.M.; Dannenmann, M.; Kiese, R.; Zechmeister-Boltenstern, S. Nitrous oxide emissions from soils: How well do we understand the processes and their controls? *Philos. Trans. R. Soc. B Biol. Sci.* **2013**, *368*, 20130122. [CrossRef]

- Zhou, M.; Zhu, B.; Wang, S.; Zhu, X.; Vereecken, H.; Brüggemann, N. Stimulation of N2O emission by manure application to agricultural soils may largely offset carbon benefits: A global meta-analysis. *Glob. Chang. Biol.* 2017, 23, 4068–4083. [CrossRef] [PubMed]
- 58. Halvorson, A.D.; Del Grosso, S.J.; Stewart, C.E. Manure and Inorganic Nitrogen Affect Trace Gas Emissions under Semi-Arid Irrigated Corn. *J. Environ. Qual.* **2016**, *45*, 906–914. [CrossRef] [PubMed]