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Article

Winter Annual Rye Seeding Date Influence on Nitrogen Recovery and Ammonia Volatilization from Late Fall Surface-Applied Manure

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Abstract: Dairy farmers in the northeast face challenges in the application of manure in fall and on-time planting of cool-season grasses to maximize recovery of residual N and nutrients released from fall applied manure. Ammonia emission from animal manure is a serious environmental concern and can be reduced if cover crop is integrated in the farming system. On-time planting of cover crops can reduce ammonia volatilization from fall, surface-applied manure, and prevents N loss to leaching. A two-year study was conducted in 2015 and 2016 to investigate if time of planting of winter annual rye (*Secale cereale* L.) along with late fall application of manure when air temperature is low can influence ammonia emission and preserve nitrogen (N) to meet the N requirement of forage rape. Three planting dates (16 September, 30 September, and 14 October) of rye cover crop with two manure application treatments including late-fall application and no manure were assessed for mitigating ammonia volatilization, and also yield and recovery of N by forage rape (*Brassica napus* L.). The highest rates of ammonia volatilization were detected in the first 24 hours after manure spreading regardless of the treatment. The result indicated that cover crop use significantly limited volatilization compared with no cover crop. The earliest planting date produced 3823 kg ha⁻¹ dry matter of winter rye cover crop that was 16 and 35 percent higher than second and third dates of planting, respectively. The manured cover crop accumulated 132 kg N ha⁻¹ when planted early. However, biomass yield of forage rape was more when planted after all cover crop treatments with manure application. Prior to forage planting, the nitrate-N content in all three soil depths (0–20, 20–40, and 40–60 cm) in the plots with manure was higher than plots with no manure. No significant differences in forage rape yield was detected among winter rye planting dates; however, forage rape planted after winter rye was higher than after no-cover crop. The results of this study suggest that when immediate incorporation of manure into soil is not feasible, establishing cover crop early and then applying manure in the late fall, is a practical management to limit nonpoint source pollution from ammonia loss.

Keywords: ammonia volatilization; forage rape; soil nitrogen; winter annual rye

1. Introduction

Fertility of agricultural soils depends in part on management to promote soil organic matter accumulation. Soil organic carbon (C) and total nitrogen (N) reflect the capability of soil to supply nutrients to plants, to mitigate greenhouse gas accumulation, to stabilize the soil surface against erosion, and to promote a biologically diverse and healthy microbial population [1–3]. Integrating

cover crops into cropping systems helps to increase organic (C) in the soil in addition to other ecological benefits such as minimizing soil erosion, improving soil structure and fertility, and restricting nitrate leaching [4,5]. Cool-season grasses such as winter annual rye and triticale are often considered as suitable cover crops for recovery of nutrients that are left after crop harvest and mineralized (N) released from fall applied manure. This is mainly due to the fast growth and deep extensive root systems of grasses [6,7]. For much of continental USA, winter rye is the most common choice for catching nitrate after a summer crop. Winter annual rye is able to capture leftover N and minimize nitrate leaching from manure during fall and winter [8]. The cold tolerance of winter rye is an advantage that allows its growth until late fall and to extend its roots to a depth of 80–90 cm or more [9].

Agriculture is known as the major source of atmospheric ammonia (NH_3), which is emitted from soils amended with manure, deposited manure by free-ranging livestock, and application of mineral N fertilizer [10–12]. The amount of N loss due to NH_3 volatilization following manure application to the agricultural land depends on many factors such as type and characteristics of the manure, the timing, amount, and method of application, and local climatic and soil conditions [13,14]. When emitted, ammonia can react with other pollutants such as the products of SO_2 and NO_x to form ammonium (NH_4^+) which causes serious health issues. In addition to the environment concern, nitrogen losses via NH_3 volatilization results in less available N for plant nutrition and diminished nutrients value of manure, thus economic losses for farmers.

The ammoniacal portion of the manure applied to the field could be transformed by several pathways. It can be volatilized as ammonia, undergoes nitrification, be taken up by plants, or become immobilized by soil microbial community. Ammonia in dairy manure is produced as a result of mineralization and urease activity and will be enhanced as temperature increased [14,15]. When manure is applied and incorporated into bare soils to avoid ammonia volatilization, the nitrogen released from manure can be lost through leaching. Thus, integrating cover crop to manured field is the key to manure management [16,17]. However, manure application must be timed to coincide with early planting of cover crops (late August to early September) to maximize N recovery before leaching or runoff occurs.

In 2005, the United States Environmental Protection Agency's (EPA) estimated that ammonia volatility from dairy and beef cattle alone accounted for about one half of the total ammonia emissions from animal wastes [18]. Furthermore, in the United States, most ammonia loss from manure occurs at the time of land application. This indicates that manure is poorly managed nationwide, and that dairy farms are prime subjects for improvements in their manure management. According to a nutrient management survey of dairy and livestock farms in Massachusetts that was conducted by the University of Massachusetts Extension in 2006, only 17% of animal operations had a manure management plan and exercising cover cropping [19]. Although immediate disking or injecting of manure into the soil can minimize ammonia volatilization, most farmers do not have the machinery needed to complete the job in one pass over a field or do not have time to return and disk the applied manure into the soil. In other situations, incorporation of manure is not possible, e.g., when manure is applied to grasslands, hay fields, pastures, or when manure is used in a no-till system [20]. We hypothesized that if for any reason the immediate incorporation of manure into the field is not possible, delaying in manure application until cool temperatures in late fall can significantly reduce the amount of ammonia volatilization.

This study aimed to investigate a management strategy for mitigating ammonia volatilization from slurry manure applied to the growing cover crops planted at different dates. Also, this research involved studying changes in the N content of cover crops, soil, and succeeding crop planted after cover crop termination.

2. Materials and Methods

2.1. Experimental Site

A 2-year field study was conducted at the Crops and Animal Research and Education Farm of the University of Massachusetts Amherst in South Deerfield, MA (42°28'37" N, 72°36'2" W, elevation 60 m) in 2014–2015 and 2015–2016. The research field is prime farmland, and the soil is a moderately well drained Winooski silt loam (coarse-silty, mixed super active, mesic Fluvaquentic Dystrudept) with a high run-off class [21] and with no manure application history. Selected soil physical and chemical characteristics of the top 15 cm were as follows: 31% clay, 56% sand; ECEC 3 to 4 cmolc kg⁻¹, pH 5.7 (l:l, soil:water), organic matter content of 1.1%, extractable N, P, K, and Ca content of 3, 8, 71, and 855 mg kg⁻¹, respectively. Weather conditions during experimental years are presented in Figure 1.

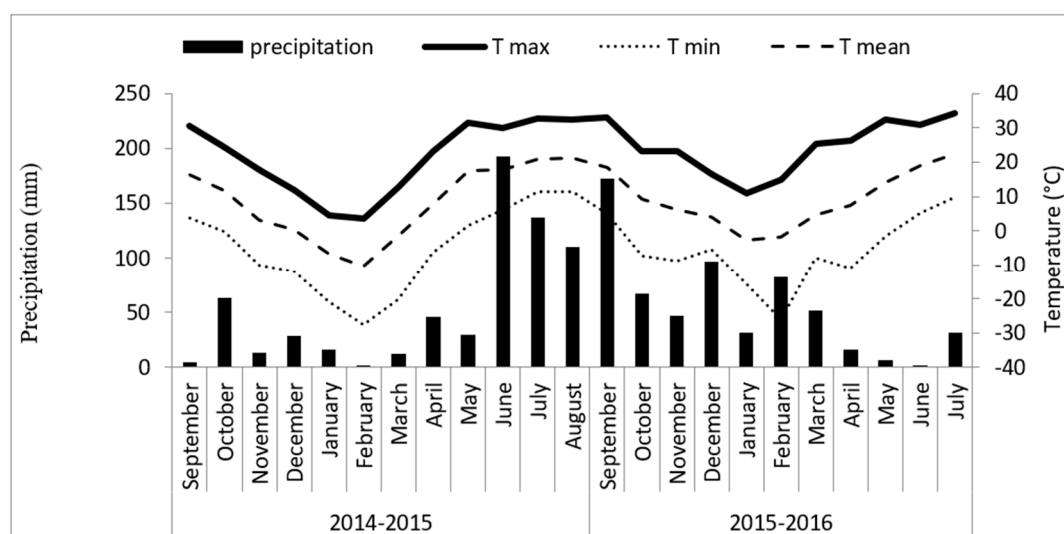


Figure 1. Monthly precipitation and average, maximum and minimum temperature during 2014–2016 growing seasons.

2.2. Experimental Design and Cultural Practices

The experimental design was a split plot, randomized complete block with three replications. The main plots consisted of three bi-weekly winter rye (*Secale cereale* L.) variety Aroostock planting dates beginning in mid-September along with a no-cover crop treatment as control. The subplots were two treatments of manure and no manure application. Plots were planted with a seven-row cone-type distributor mounted on a double-disc opening planter. Cover crop row spacing was 0.18 m. Plots were 3 m wide and 6 m long. Winter annual rye was drilled at the rate of 112 kg seed ha⁻¹. In spring, winter rye cover crop was terminated by an application of glyphosate [N-(phosphonomethyl) glycine] at 0.84 kg ha⁻¹. Plots in spring were disked, which left approximately 30% of the overwintered residue cover on the soil surface. Forage rape (*Brassica napus* L.) was planted at 5.5 kg ha⁻¹ pure live seed in late April and harvested in early August. In the current study, no supplemental N was applied to forage rape as it was assumed that gradual release of N from decomposing cover crop and mineralization of fall manure application would be sufficient. No irrigation was applied since it is not a common practice in Massachusetts [6].

2.3. Manure and Ammonia Volatility

In each year, slurry manure was obtained from nearby Mount Toby Dairy Farm in Sunderland, Massachusetts and applied in cold weather, but on unfrozen ground, on 20th December with the purpose of minimizing ammonia emission compared with traditional fall manure application to the cover crops planted in mid-September through mid-October. Manured plots were monitored for

ammonia volatilization immediately after spreading. A sample of manure used in this study was frozen and sent to the University of Maine Analytical Laboratory (Orono, Maine) for analysis (Table 1).

Table 1. Characteristics of slurry manure used in this study. Dry-matter (DM), total $\text{NH}_4\text{-N}$, total N (TN), and pH in two years of the experiment.

	DM (kg ha^{-1})	$\text{NH}_4\text{-N}$ (kg ha^{-1})	TN (kg ha^{-1})	pH
2014	94	61	163	7.1
2015	71	54	137	6.8

Manure was applied uniformly at the rate of $56,000 \text{ L ha}^{-1}$ [22]. Immediately after surface application, a glass chamber with a sampling jar that contained 50 mL 0.02M H_2SO_4 was placed over the manured land. The ammonia volatility measuring chambers covered a 0.06 m^2 surface area with one liter of manure in the center and were moved to a new location at the beginning of each hour of sampling, so that the manure being sampled was exposed to ambient conditions and not influenced by chamber conditions (Figure 2).

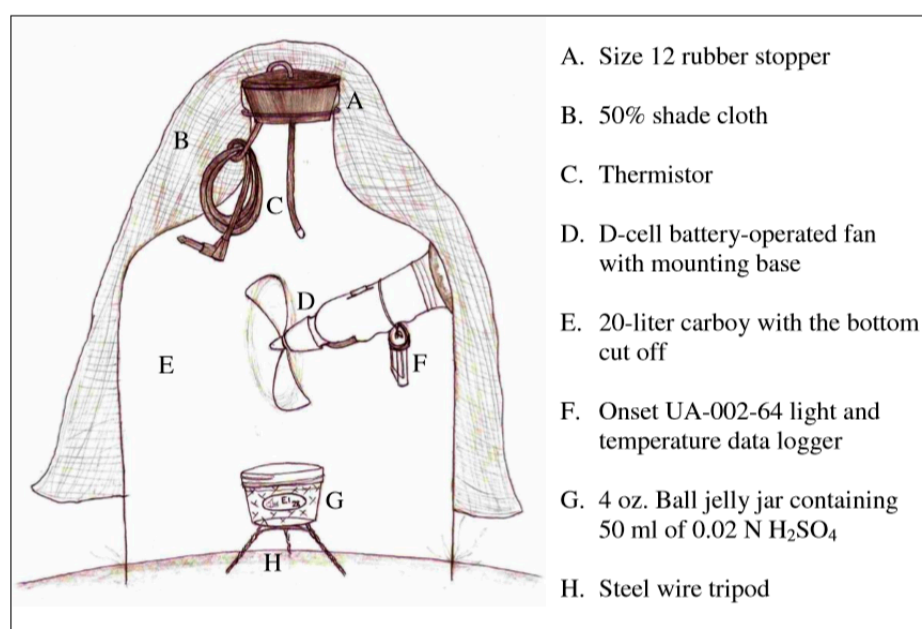


Figure 2. Schematic representation of apparatus used for collecting $\text{NH}_3\text{-N}$ from manured soils.

At each measurement, the temperature and time for each chamber was recorded. The acid containing sampling jars were placed on a small tripod in the center of each sampling area. The battery-operated fans inside the chambers were turned on and a glass chamber was placed over the sampling jars and twisted into the surface to a depth of approximately two cm into the soil. After an hour, the chamber was removed, and the lid on the sampling jar was replaced. These steps were repeated for all experimental plots over a period of 73 hr. The emitted ammonia dissolved in the H_2SO_4 sampling jars was measured by flow injection analysis (Lachat Instruments QC 8500 Spectrophotometer), using Lachat method 12-107-06-2-A modified for a sulfuric acid matrix [23]. Cumulative $\text{NH}_3\text{-N}$ volatilization was calculated by adding consecutive samplings.

2.4. Cover Crop and Soil Nitrate Measurements

Winter rye cover crop biomass was harvested from an area of 0.18 square meters of the center rows, using a hand mower (GS model 700, Black and Decker Inc., Towson, MD, USA) at the soil surface in early April. Biomass samples were dried in a forced-draft oven at $65 \text{ }^\circ\text{C}$ to constant weight. Dried

samples were weighed for dry matter and then ground using a heavy-duty grinder. Total N was measured by Kjeldahl procedures and by colorimetric flow injection analysis [24,25].

Before manure application, soil samples were taken to determine soil nitrate in early December and also just before forage rape planting in April. The soil samples for nitrate measurement were taken only from the mid-September (earliest) cover crop planting and no cover crop plots. Three composite soil cores (2.5-cm diam. and 0–20, 20–40, and 40–60 cm depth) were taken at least 0.5 m away from the plot borders and previous sampling holes. Soil samples were placed in a cooler and transported to the laboratory. Samples were passed through a 2-mm mesh sieve, and stored at 4 °C for about two weeks prior to chemical analyses. Soil nitrate was extracted with 0.01 M CaCl₂ by shaking for 15 min and filtering, and the resulting filtrate was analyzed by colorimetric flow injection analysis [25].

2.5. Statistical Analysis

Data were processed by analysis of variance (SAS, 9.1.3, The SAS Inst) [26]. The normality of the distribution of the data was tested by Kolmogorov Smirnov Test [27]. No transformation was applied since the distribution was normal. If the treatment effect was significant by F-test ($p \leq 0.05$), mean separation was performed by Duncan's New Multiple Range Test. The response to applications was partitioned into linear and quadratic trends if the effect of the treatment was significant [28].

3. Results and Discussion

3.1. Ammonia Volatilization

Figure 3 illustrates the pattern of NH₃-N loss during 73 h after manure application. The highest rates of ammonia volatilization were detected in the first 24 h after spreading on all treatments. Manure applied to the soil with cover crop significantly emitted less NH₃-N compared to no cover crop soil (Figure 3). Figure 3 also indicates that ammonia loss was smaller with mid-September planting date than delayed planting. These trends agree with the result from another experiment by [29,30] found that 57–77 percent of total NH₃-N emission occurred in the first 24 h. Similarly, [31] concluded that 85 percent of NH₃-N volatilization occurred within 24 h with surface applied manure. Ammonia volatilization could continue at significantly much lower rates past the 120–150 h sampling period.

The effectiveness of cold temperatures on ammonia volatility from surface applied manure have been investigated in earlier research at the University of Massachusetts Research Farm [16]. Results indicated that ammonia loss from surface applied manure in December was about one-fifth of the ammonia loss from manure applied in September. Application of manure on cover crops in late fall when air and soil temperatures is low, restricts N losses due to ammonia volatility while cover crop roots capture soil N, thus lowers nitrate leaching. Other reports confirmed the close positive correlation between ammonia emission rates and temperature [32,33].

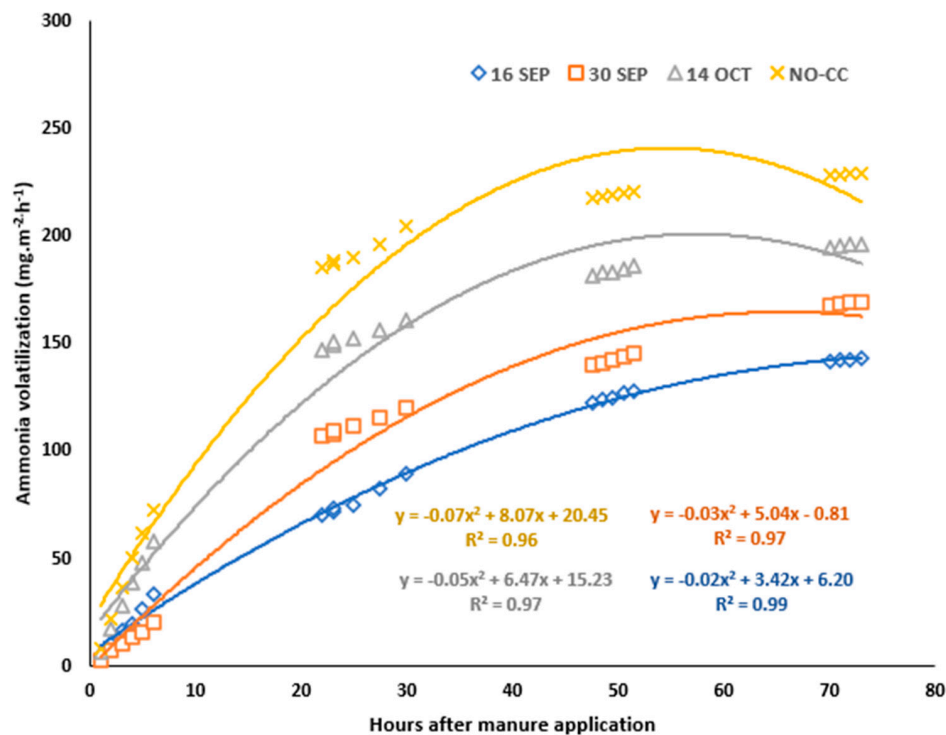


Figure 3. Ammonia volatilization as a function of time after manure application to the bare soil (no cover crop) and to the cover crops planted at different dates. SEP, OCT, and NO-CC are September, October, and No cover crop, respectively.

3.2. Cover Crop Biomass and Nitrogen Accumulation

Winter rye cover crop responded positively to the surface applied manure and produced over 28% higher biomass compared to the cover crops in none-manured plots (Table 2). Winter rye that was planted on September 16 (earliest planting date) produced 3823 kg ha⁻¹ dry matter that was 16 and 35% higher than second and third dates of planting, respectively. Earlier reports similarly have been emphasized on the importance of early planting of fall-sown cover crops for maximizing biomass production [34–39]. As a general rule, the higher cover crop biomass, the greater ecological services, including N recovery can be expected [35]. Total N content in cover crop tissues is important, since the accumulated N in the residues will be gradually released into the soil and potentially can be available to the succeeding crop. In the current study, accumulation of N in winter rye cover crop shoots followed a decreasing linear trend in response to the planting date (Table 2).

Averaged over cover crop planting dates, winter rye that received manure accumulated 109 kg N ha⁻¹, whereas non-manured cover crops contained 78 kg ha⁻¹. Nitrogen removal by cover crops in manured and non-manured plots also depended on their planting date. For example, the non-manured rye planted on 16 September removed 23% less N compared with the manured plot at the same date of planting.

Table 2. Winter rye cover crop biomass prior to termination in spring and its total nitrogen content of shoots as a function of planting date and surface manure application.

	Rye – M	Rye + M	Mean
Date of planting		Cover crop biomass, kg ha ⁻¹	
16 September	3367	4280	3823a
30 September	2613	3792	3202b
14 October	2020	2995	2507c
Mean	2667b	3689a	
Trend	Q **	Q **	Q **
		N content, kg ha ⁻¹	
16 September	102	132	117a
30 September	75	107	91b
14 October	57	87	72c
Mean	78b	109a	
Trend	L **	L **	L **

Means followed by different letters in rows or columns are significantly different by Duncan's New Multiple Range Test ($p = 0.05$). The LSD_(0.05) for the interactions of biomass is 247 and for total N is 18. L, linear and Q, quadratic; ** $p \leq 0.01$. Rye + M: Rye plus added manure and Rye-M: Rye with no manure.

When rye planting was delayed until 14 October, the difference in N accumulation increased to 34% (Table 2). The smaller difference between N content of cover crop in the earliest date of planting than those in delayed planting dates could be in part due to more availability of residual N left from previous crop. As cover crop planting was delayed until 14 October, some residual N was lost possibly due to leaching, thus less N was available to cover crop in non-manured plots. The results of the current study confirmed that winter rye has a great potential for capturing residual N from fall manure fields, which otherwise could have been lost to the environment. Nitrogen removed by cover crops from soil can potentially provide substantial amount of N to the succeeding crop [4,40].

3.3. Soil Nitrate

Nitrate-N levels in the soil profile were affected by manure application and winter rye cover crop (Figure 4). The figure shows the concentration of nitrate at three soil depths in the plots of the earliest winter rye planting date and no-cover crop with manure and without manure application. On average, there was about 60% more nitrate-N in soil amended with manure. In April, the nitrate-N content in all three soil depths in the plots with manure application were higher than plots with no manure application. The soil nitrate-N level in winter rye plots in the fall, before manure application, was more constant at all soil depths compared with no-cover crop plots at similar depths. The major difference between plots with or without cover crops is that in plots with no-cover crops, the lower nitrate-N indicates some nitrate was lost to leaching below the soil-sampling depth, whereas in plots with cover crops, more nitrate was taken up by plant roots and accumulated in the cover-crop tissues. Several studies showed that winter cover crops can contribute indirectly to overall soil health by accumulating nutrients before they can leach from the soil profile or, in the case of legumes, by adding N to the soil [8,34,41,42]. Soil nitrate amounts in the spring are the portion of the soil N that is available for plant uptake (Figure 4). Leaching transports nitrate below the crop root depth. A very significant portion of nitrate leaching occurs in fall, winter, and early spring, when the amount of nitrate in the soil solution is more than crop requirements or if there is no crop to absorb it [43–45]. Surface application of manure in the late fall when air and soil temperatures have decreased, limits nitrogen loss due to reduced ammonia volatility. The cold temperatures restrict potential for N mineralization, nitrification, and ammonia volatilization. In a three-year study conducted by [46], a late-fall surface application of liquid dairy manure had less ammonia volatilization than an early fall application and had amounts of volatilization equal to that of spring applications of manure.

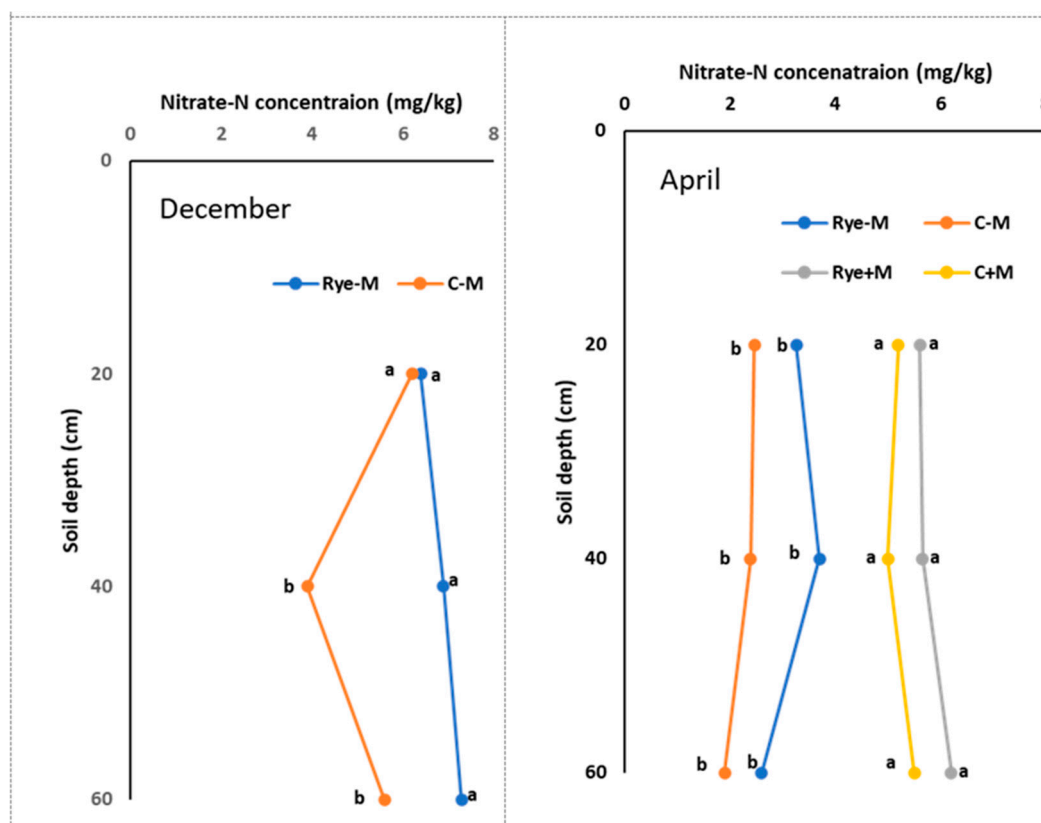


Figure 4. Nitrate-N levels in soil profile as affected by manure application and cover crop. Letters note separation of means by Duncan's New Multiple Range Test, $p = 0.05$. Date of soil sampling (April) and (December). Rye cover crop added manure (Rye + M), Rye cover crop with no manure (Rye-M), No cover crop with added manure (C + M) and no cover crop with no manure (C – M).

The results of this study suggest that when immediate manure incorporation into soil is not feasible, establishing cover crop early and then applying manure in the late fall, is a practical management to limit nonpoint source pollution from ammonia loss. The established cover crops will also reduce nitrate leaching and lower the cost of fertilizer purchases for growers. A field study by [16] showed that greater N retention in soil below plots spread with manure in November or December may be due to the inactivity of nitrifying bacteria in cold temperatures and thereby had less leaching than with September or October applications.

Furthermore, manure application in late fall produced less nitrate leaching than an early fall application and produced amounts of leaching equal to that of spring applications of manure.

The results of this study suggest that when immediate incorporation of manure into soil is not feasible, establishing cover crop early and then applying manure in the late fall, is a practical type of management to limit nonpoint source pollution from ammonia loss. The established cover crops will also reduce nitrate leaching and lower the cost of fertilizer purchases for growers.

3.4. Forage Rape Yield

Application of manure and cover crop planting dates both had significant influence on forage rape biomass. Averaged across all four cover crop treatments, forage rape produced approximately 40% higher biomass when plots were amended with manure. Regardless of cover crop planting date, forage rape yielded about 4 Mg ha^{-1} in manure plots compare with only 3 Mg ha^{-1} in non-manured plots (Figure 5). Greater yields may be attributed to greater available N due to a reduction in ammonia loss from manure by the cover crops and to a reduction in nitrate leaching from the soil [47,48]. Also, winter rye was effective in accumulating soil N and fall-applied manure N and making this available to

forage rape in the following growing season. Although no significant differences in forage rape yield occurred with different winter rye planting dates, the yield response in forage rape planted after winter rye was higher than after no-cover crop. A possible explanation for the results is that in no-cover crop plots some of the nitrate may have been lost through leaching, whereas the cover-crops accumulated N, and the decomposing cover crop residues during the growing season would provide a slow-release source of N for the subsequent forage crop [49–51]. It has been suggested commonly that use of a cover crop following manure application will result in N sequestration by the cover crop and subsequent mineralization and release to the following crop [52,53]. Delaying manure application to late fall may provide more available N during the growing season rather than applying in the early fall with cover crops [16].

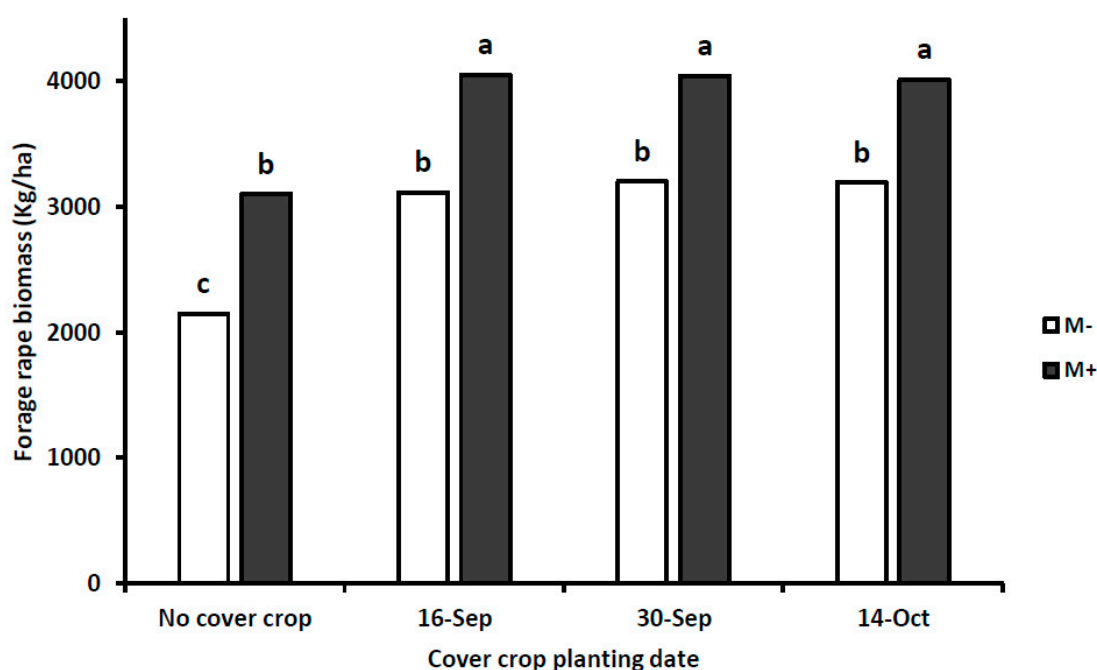


Figure 5. Forage rape yield as a function of cover crop planting date and manure application. Letters indicate mean separation by Duncan's New Multiple Range Test ($p = 0.05$). Rye cover crop added manure (M+) and Rye cover crop with no manure (M-).

4. Conclusions

Delaying the planting of winter cover crop resulted in a significant reduction in its biomass, which is required for ecological benefits. In no-till systems or when cover crop is planted immediately after crop harvest and manure is surface applied in fall, a majority portion of ammonia-N is volatilized within 73 h. To avoid N losses in the form of ammonia volatilization or leaching, delaying manure application until late fall should be considered as an environmentally- and cost-friendly management approach. Early planting winter rye also resulted in accumulation of considerable amount of N in cover crop biomass that gradually released during non-fertilized forage rape growing season.

Author Contributions: This work is a combined effort of all the authors; conceptualization and designing the experiments, P.A. and S.H.; performing field experiments, P.A., Z.E.B., O.R.Z.; chemical analyses, P.A. and M.H.; statistical analysis of data, and producing the presentation tables and figures, P.A., O.R.Z., S.H.; writing the original draft with contributions from all of the authors, P.A. and O.R.Z.; reviewing and editing the whole manuscript, M.H., S.H., A.B. All authors have read and agreed to the published version of the manuscript.

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