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Reducing Ammonia Emissions from Digested Animal Manure: Effectiveness of Acidification, Open Disc Injection, and Fertigation in Mediterranean Cereal Systems

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Abstract

Ammonia poses a risk to human health and terrestrial and aquatic ecosystems. In Spain in 2022, the agricultural sector was responsible for 97% of ammonia emissions to the atmosphere, with the application of animal manure as fertilizer accounting for 24.4% of these emissions. The search for effective mitigation strategies in the application of animal manures is imperative to support the implementation of policies that contribute to the sustainability of the agricultural sector. The aim of this study is to evaluate three digestate application techniques, namely, acidification, open disc injection, and fertigation, in a wheat–maize rotation and compare them to traditional trail hose application. In spring wheat topdressing, acidification is the most efficient method for reducing ammonia emissions, followed by disc injection and, finally, fertigation. In the summer base dressing to maize, acidification is the best method, with more than 70% reduction compared with trail hoses. In terms of both base dressing and side-dressing fertilization, the most efficient method is fertigation, with a 70% reduction, followed by acidification and disc injection (>25%). Although the three methods reduce ammonia emissions, they have certain drawbacks: fertigation requires previous solid/liquid separation, acidification requires ad hoc equipment, and disc injection requires high mechanical traction.

Keywords: digestate; ammonia; disc injection; fertigation; acidification

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1. Introduction

Spain, with more than 34 million heads, is the leading country in Europe in terms of pig production [1]. The regions of Aragón and Catalonia in northeastern Spain account for 52% of this population [2]. In recent years, the anaerobic digestion of slurry has become increasingly popular, emerging new farm facilities that produce digestate. Both raw slurry and digestate are excellent fertilizers for crops; however, if not applied correctly, they can have negative environmental consequences, such as nitrate leaching [3,4] and the emission of greenhouse gases, such as methane and nitrous oxide [5,6] and ammonia, to the atmosphere [7,8]. In 2022, the agricultural sector in Spain was responsible for 97% of ammonia emissions. Although Spain has complied with its ammonia emission reduction commitments under the Gothenburg Protocol in recent years [9,10], further reduction remains necessary given the significant adverse effects of ammonia, which pose risks to human health [11] and contribute to environmental degradation [8,12].

From a legislative perspective, the National Emission Ceilings Directive (Directive 2016/2284), which establishes commitments for EU Member States to reduce ammonia emissions, and the implementation of best available techniques (BATs) to reduce the environmental impact of livestock farming in Spain [13] both affect the management of manure on farms and its application to field crops. Reducing nitrogen inputs to crops and optimizing fertilization are dominant factors in decreasing ammonia emissions from both mineral and organic fertilization [14,15].

The processes that control ammonia emissions from fertilizers are numerous and complex, and they have been widely studied. Examples include the metanalyses of Hurtado et al. [15] and Søgaard et al. [16], with the development of the ALFAM model (https://projects.au.dk/alfam//, (accessed on 16 July 2025), and the review of Sommer et al. [17]. Hurtado et al. [15], using information from 234 field experiments in Mediterranean climate areas, reported that the N rate was the most influential variable affecting ammonia emissions, followed by fertilizer type, with pig slurries and urea being the two main emitters, associated with their high pH values. Søgaard et al. [16] developed the ALFAM model, with data from more than 80 experiments in Europe to model the factors that significantly drive ammonia emissions when animal manure is applied to soils; this work is in an active state, with new versions being developed and databases being expanded [18,19]. Sommer et al. [17] reviewed the importance levels of various processes that have not been previously considered, affecting ammonia volatilization when slurry is applied to the soil, including the turbulent and molecular diffusion of ammonia in the atmosphere, chemical processes affecting the pH of slurry, and physical processes controlling the movement of slurry into the soil.

Thus, the main factors driving ammonia emission from animal slurries when applied to the field are atmospheric processes, mainly solar radiation, temperature and wind speed [16,17]; processes that control the pH of the slurry [16,18,20–25]; application methods that control the movement of slurry into the soil and the exposed area [16,26]; and the composition of the slurry, in particular its ammonia and dry matter content [7,16].

Application methods of liquid animal manure that reduce ammonia emissions include acidification, injection, and fertigation. Acidification reduces the solution pH, reducing the amount of free ammonia in solution [27]; however, although acidification is used to reduce ammonia emission from housing and open storage ponds, it is scarcely used in field applications, except in some countries, such as Denmark and Germany, even with the high potential to abate NH_3 emissions [23]. The long-term effects of acidified slurry application on soil are not well known, although information from a short-term experiment has revealed that the application of acidified slurry materials to soil has no negative effects on enzymatic activity and soil characteristics [28]. In the injection system, the digested slurry is injected into the soil increasing the slurry–soil contact and reducing the surface area exposed to the atmosphere [22]. Fertigation combines several factors that contribute to reducing ammonia emissions: a decrease in dry matter content associated with the necessary prior separation to allow injection in irrigation systems, an additional decrease in dry matter and ammonia concentration through dilution with irrigation water, rapid infiltration of digestate into the soil with water which reduces slurry exposure to the atmosphere [29,30], N splitting, and a reduction in the N rate [15]. Acidification and injection techniques have been evaluated and compared under different edaphoclimatic conditions, mainly using cattle slurry. However, available information about the potential of fertigation to reduce ammonia emissions is scarce.

Ammonia emission from field-applied digestate has rarely been studied, and a review by Pedersen and Hafner [31] revealed the high variability within available data as well as high uncertainty due to the lack of measurements. Management of anaerobic digestion involves the addition of different substrates that increase dry matter content and, along with the increase in the pH during the process, enhance the potential to emit ammonia from the digestate produced [32]; however, Efosa et al. [33] reported that even when ammonia emissions tended to be higher from digestate than from untreated slurry, the differences were not statistically significant. The evaluation of emissions and efficient methods to mitigate emissions from the application of digestate to land are needed to support the implementation of policies that contribute to the sustainability of the agricultural and livestock sectors, improving the environment and reducing risks to human health.

Low-emission technologies that efficiently reduce ammonia emissions after the field application of raw slurry are expected to have similar potential for mitigating ammonia emissions from digested slurry. Thus, in this work, we focus on a preliminary evaluation of the efficiencies of different application techniques for reducing ammonia emissions when digested pig slurry is applied to land. Three application methods are evaluated: acidification, open disc injection and fertigation in spring and summer applications. These three methods are compared to band application with trailing hoses, which is the traditional application method in the study area. The advantages and limitations of the three field application techniques are also presented.

2. Materials and Methods

The experiment was conducted at the Agronomic Centre La Melusa (Tamarite de Litera, Huesca) and included four application techniques, acidification, open disc injection, fertigation and band application with trail hose. Acidification, open disc injection and trail hose (reference technique) were deployed in three plots (surface area of approximately 1 ha) irrigated with fixed sprinkler coverage (18 m × 18 m), and fertigation was installed on a 6.3 ha pivot (Figure S1). Between two and four monitoring stations for measuring air ammonia concentration were installed within each plot to obtain replicate estimates of ammonia emissions.

The experiment was carried out in a wheat–maize rotation during 2022. Wheat was fertilized exclusively with digestate at topdressing (spring application). Maize was fertilized with digestate before sowing (summer application), and complemented with mineral fertilizer at topdressing, except in the fertigation system, where digestate was applied only at topdressing (summer application) to cover all of maize's nitrogen requirements.

In the reference and acidification plots, digestate was applied using 9-m-long trail hose machinery with 36 hoses. The disc injector had a 4.25 m working length with 20 discs and associated tubes that deposited the digestate into the slots created by the discs (3 cm depth). The pivot was fitted with rotator nozzles (Nelson D3000) that could provide a large droplet size and low evaporation and wind-drift losses, with a nozzle spacing of 1.4 m being positioned 0.4 m above the soil surface and operating at a pressure of 0.4 bar (Figure S2). Next to the pivot plot, two 50 m^3 cylindrical tanks for storing the digestate and its liquid fraction, a separator to filter the solid fraction of the digestate, and an injection pump to inject the liquid fraction of digestate into the irrigation system were installed (Figure S3). The separator consisted of a filtering screen ramp and a screw press with a mesh size of 250 μm, with filtration rates of 6–7 m^3 per hour. The liquid fraction of the digestate obtained after separation was suitable for injection into the pivot system, avoiding clogging issues [34].

The digestate used in the trials came from a biodigester located on a sow farm where, in addition to slurry, a small amount of maize silage was used to increase the methanation potential. The target application rate of digestate as topdressing for wheat and basal application of maize was set to 170 kg total N ha^{-1}, which is the typical rate used for these crops in the area according to crop demands and legal restrictions (Directive 91/676/CEE).

On the basis of previous analyses of the digestate (2.28 kg total N m^{-3}), the target digestate volume to apply was set to 70 m^3 ha^{-1}.

For acidification, 100 L of sulfuric acid was added to 20 m^3 of digestate; this ratio has been established in a previous small-scale experiment in the laboratory to decrease the digestate pH to 6 [27]. The initial digestate pH ranged from 8 to 8.2 and decreased to 6.5–6.9 after acidification (Table S1). Slurry pH was measured at ambient temperature using a pH meter (MW102; Milwaukee Instruments Kft., Szeged, Hungary). To determine digestate application rates, the GPS coordinates of the corners of the area treated by each application tank were recorded, and a digestate sample from each tank was taken for laboratory analysis. In the case of fertigation, the volume of digestate applied was controlled at each fertigation event using a height meter installed in the tank containing the filtered digestate, and samples were taken periodically for laboratory analysis.

The acidification (AC), disc injection (D), and fertigation (FR) plots were adjacent, and to avoid interference in the ammonia measurements [35], at least seven days were left between slurry application to adjacent plots (Figure S1). This interval was selected because NH_3 volatilization typically peaks within the first 4–5 days after application [20,36–38]. In spring, digestate was applied to wheat at the tillering stage on 10 March (acidification), 24 March (reference), and 22 March (disc injection) of 2022. For fertigation, digestate applications were conducted between 11 April and 29 April (Table S2). In summer, basal digestate application to maize was performed on the wheat stubble after straw removal on 18 July (disc injection), 19 July (reference), and 25 July (acidification) (Table 1). Fertigation digestate applications began on 17 August (2-leaf stage) and ended on 16 September (Table S3).

Table 1. Area, dates of digestate and urea applications and periods of ammonia concentration monitoring for the four application techniques in spring and summer applications.

	Spring Application (Wheat)			**Summer Application (Maize)**		
	Area ha	**Date**	**NH3 Control Period**	**Area ha**	**Date**	**NH3 Control Period**
	Digestate					
Reference	0.71	24/03	24/03–05/04	0.85	19/07	19/07–27/07
Open Discs	0.86	22/03	22/03–30/03	0.95	18/07	18/07–26/07
Acidification	0.60	10/03	10/03–22/03	0.73	25/07	25/07–31/07
Fertigation	6.27	11/04–29/04	8/04–3/05	6.27	17/08–16/09	17/08–21/09
	Urea					
Reference				0.85	31/08	31/08–13/09
Acidification + Open discs				3.47	31/08	31/08–13/09

In the acidification, disc injection and reference plots, urea was applied as maize topdressing at the 4-leaf stage (31 August 2022) at a rate of 160 kg N ha^{-1}, which is the usual rate applied by farmers in the area to this crop.

2.1. Sampling and Determinations

2.1.1. Soil

Soil was sampled after the wheat harvest (0–30 cm) on 4 July 2022, and after the maize harvest (0–30, 30–60, 60–90 cm) on 16 November 2022. Soil samples were taken from at least four points in each plot, with the 0–30 cm layer being a composite of at least three subsamples. A soil subsample was oven dried (105 °C) to determine the soil gravimetric water content, and nitrate and ammonium concentrations were determined in 1:3 soil extracts (10 g of fresh soil/30 mL of 2 N KCl, [39]) by colourimetry (UNE 77306:199972) using a segmented flow analyser (AutoAnalyser 3, Bran + Luebbe, Norderstedt, Germany).

2.1.2. Ammonia Emissions

To calculate ammonia emissions, the backwards–Lagrangian–stochastic model (bLS) was selected [40]. The model inferred the ammonia flux from an emitting surface using NH_3 concentrations measured in the air upwind (background concentrations) and downwind or within the of the emission surface, both at a single height, the surface roughness length (or the height where the wind speed is zero), wind speed, and wind direction [41]. This methodology was evaluated in the study area by Herrero et al. [42], showing very good agreement with the micrometeorological Integrated Horizontal Flux (IHF) method using passive flux samplers, which is the reference method established by the VERA protocol [43] for verifying ammonia emissions from the application of animal manures to soils.

For modelling, the free software WindTrax v.2.0.8.9 (Thunder Beach Scientific, Halifax, NS, Canada) was used. WindTrax releases particles backwards from the measuring points and tracks their paths to determine the origin and emission flow rate from a known emitting surface, always considering the wind speed and direction. This process is conducted stochastically, simulating the random and turbulent movement of the atmosphere to trace the unique movement of each particle. Emissions from the emitting surface are calculated so that the ammonia concentrations estimated by the model at the sampling points match the measured values.

Ammonia concentrations in the air were monitored using ALPHA® passive samplers developed by the Centre of Ecology & Hydrology, Edinburgh, United Kingdom) [44]. Alphas were placed at a height of 1.5 m above the emitting surface: the soil surface for spring digestate topdressing, summer digestate basal application and urea topdressing application, and the crop canopy for fertigation. Around each plot, at least two monitoring stations were established to determine background ammonia concentrations. Within the plots, two stations were established in spring (3 for fertigation) that were increased to four for summer. Each monitoring station consisted of a mast with a plate holding three downwards-facing ALPHA® samplers (Figure S2). ALPHA® samplers were replaced every 24 h during the first four days following digestate or mineral fertilizer application, after which the sampling frequency was reduced, the measurement periods are indicated in Table 1. Ammonia emissions after urea topdressing were estimated jointly in the adjacent disc and acidification plots (AC + D) using four monitoring stations, two in each plot. The positions of the ALPHA samplers were mapped by GPS coordinates.

The Alpha fibre filters were impregnated with a (13% m/v) citric acid–methanol solution, and after exposure, the trapped ammonium was extracted with 3 mL of deionized water [42]. Ammonium concentration in the extracts was determined following the salicylate method with nitroprusside [45] with a segmented flow analyser (AutoAnalyser3, Bran + Luebbe, Norderstedt, Germany).

A weather station was installed next to the plots, and the wind speed and direction were recorded every 30 min at a height of 1.5 m.

The NH3 emission flux for each measurement period was calculated using 30 min interval WindTrax runs following the methodology of Herrero et al. [42]. The inputs for each run included average half-hour wind speed, the average ammonia air concentration measured in the masts within the plot during each sampling period, and the average ammonia air concentration measured at one of the background masts selected according to the prevailing upwind direction. The average emission flux for every period was obtained by summing the 30 min fluxes.

2.1.3. Harvest

To assess wheat yield, a 0.5 m × 0.5 m area was manually harvested at four points in each plot near the mast locations on 4 July, followed by mechanical harvesting on 6–7 July. Straw removal was interrupted by a storm and resumed on 14 July, which delayed the start of the summer experiment.

In maize, two 1-metre-long rows were manually harvested at four points near the mast locations on 14 December for acidification and pivot plots and on 20 December for disc and reference plots.

The grain yield, grain moisture (PM-600 grain moisture, Kett, Tokyo, Japan), and fresh and dry biomass weights of the plant samples were determined. The total nitrogen concentration was analysed in grain and plant samples of wheat and maize (TruSpec CN, LECO, St. Joseph, MI, USA). The grain yield was reported on the basis of a moisture content of 120 g kg^{-1} for wheat and 140 g kg^{-1} for maize.

2.2. Data and Statistical Analysis

Ammonia emissions were estimated individually for each mast using the ammonia concentration measured at that mast. These values were used as replicates to compare the different application methods using ANOVA. The average emission value for each plot was estimated considering the ammonia concentration measured at all the masts in the plot. Nitrogen use efficiency was calculated as the ratio between the amount of nitrogen taken up by the crop and the amount supplied through fertilization. This calculation was performed separately for each crop.

The effects of different application methods on ammonia emissions, crop yield, nitrogen uptake, and nitrogen use efficiency were assessed using analysis of variance (ANOVA). Differences between treatments were established using Tukey’s test ($p = 0.05$). Statistical analysis was performed using Statgraphics Centurion version 18.1.10 (Statgraphics Technologies, Inc., The Plains, VA, USA).

3. Results

3.1. Digestate Application

In the wheat crop, the amounts of nitrogen applied in the reference and disc injection systems (198.8 kg N ha^{-1}) were close to the target dose (170 kg N ha^{-1}), whereas the amounts applied in the acidification system (104.8 kg N ha^{-1}) and fertigation (41.7 kg N ha^{-1}) were considerably lower than the theoretical doses (Table 2). In the maize crop, although the volumes of digestate applied in the reference and disc systems matched the planned volumes (70 m^3 ha^{-1}), the amounts of nitrogen applied (126.1 and 105.4 kg N ha^{-1} for the reference and disc systems, respectively) were lower than expected because the total nitrogen concentration of the digestate was lower than anticipated: 1.16 kg N m^{-3} (reference) and 1.71 kg N m^{-3} (disc system). For acidification, the application process was hindered by the long time required to acidify the digestate in the storage tanks and the posterior load of digestate into the field application tank, resulting in lower N doses than planned, especially for maize, where the total nitrogen concentration of the digestate was particularly low (1.16 kg N m^{-3}; Table 2). For fertigation in the wheat crop, injection was delayed because of the proximity of the pivot to the acidification and disc plots, which could have caused interference in air ammonia concentration measurements if simultaneous application occurred. Additionally, fertigation was hampered by rainfall (Figure 1), which prevented the usual irrigation of the crop and hence the injection of digestate into the system. An initial injection of 60.0 kg N ha^{-1} using ammonium nitro sulfate was required before digestate application could commence. Thus, in the wheat crop, 41.7 kg N ha^{-1} was applied via digestate, and a total of 101.7 kg N ha^{-1} was accounted for, including the ammonium nitro sulfate application (Table S2). For maize, the dose applied via fertigation was 142.0 kg N ha^{-1}, and it was applied after crop establishment in the field (Table S3).

Table 2. Digestate application: application area, digestate rate, average total Kjeldahl nitrogen (TKN, kg ha^{-1}) and total ammoniacal N (TAN, kg ha^{-1}) concentrations and applied N rate for the four application techniques in the two periods spring and summer. Values in parentheses indicate the standard error.

			Concentration		**N Rate**	
	Area m^2	**Digestate Rate** m^3 ha^{-1}	**TKN** kg m^{-3}	**TAN** kg m^{-3}	**TKN** kg ha^{-1}	**TAN** kg ha^{-1}
			Spring (wheat)			
Reference	0.71	71.6	2.78 (±0.01)	1.35 (±0.01)	199.0 (±0.4)	96.2 (±0.4)
Open Discs	0.86	73.6	2.70 (±0.07)	1.35 (±0.01)	198.8 (±5.2)	99.2 (±0.6)
Acidification	0.60	52.9	1.98 (±0.06)	1.30 (±0.01)	104.8 (±3.2)	68.8 (±0.0)
Fertigation	6.27	29.8	1.36 (±0.02)	1.08 (±0.03)	41.7 (±0.6)	31.3 (±0.8)
			Summer (Maize)			
Reference	0.85	73.9	1.71 (±0.06)	1.18 (±0.06)	126.1 (±4.7)	87.4 (±4.4)
Open Discs	0.95	66.4	1.59 (±0.15)	1.21 (±0.02)	105.4 (±10.2)	80.4 (±1.4)
Acidification	0.73	54.7	1.16 (±0.03)	1.04 (±0.03)	63.5 (±1.6)	56.9 (±1.6)
Fertigation	6.27	108.8	1.35 (±0.10)	1.08 (±0.02)	142.0 (±10.7)	118.8 (±2.3)

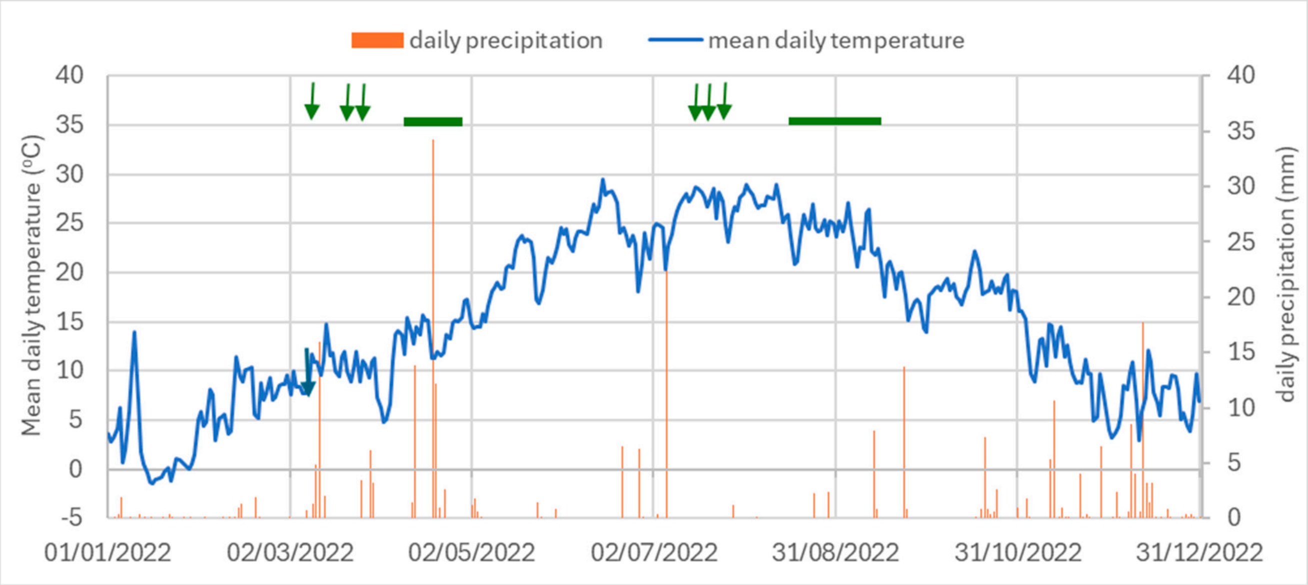


Figure 1. Mean daily temperature and daily precipitation in the meteorological station La Melusa (SIAR net HU-04) in year 2022. Green arrows and horizontal lines indicate the time of digestate application to the fields.

3.2. Yield and Soil Mineral Nitrogen

No significant effect of the application system was observed on the wheat yield or nitrogen uptake (Table 3). The average wheat yield was 5729 kg ha^{-1}, with an average nitrogen uptake of 191 kg N $^{-1}$. Maize grain yield and N absorbed in the grain were greater under acidification than in the reference method, although no differences were observed in total nitrogen uptake. The average yield was 6656 kg ha^{-1}, with a nitrogen uptake of 156 kg N ha^{-1}. The soil in the reference plot was slightly saline ($CE_{1:5}$ = 0.61 dSm^{-1}), which could have negatively affected the grain yield of the two crops.

Table 3. Grain yield, grain N concentration, amount of N in grain, N uptake by the crop and nitrogen use efficiency (NUE) under the different application methods in the wheat–maize rotation. Values in parentheses indicate the standard error.

	Grain Yield (kg ha^{-1})	**Grain N Concentration (%)**	**N in Grain (kg N ha^{-1})**	**N Uptake (kg N ha^{-1})**	**NUE**
			Wheat		
Reference	4853.3 (±533.2)	1.94 (±0.11)	85.4 (±8.2)	167.6 (±18.0)	0.84 a
Open Discs	5530.7 (±850.2)	1.59 (±0.05)	81.4 (±14.7)	168.8 (±30.4)	0.84 a
Acidification	5870.6 (±679.6)	1.85 (±0.22)	100.3 (±17.3)	220.3 (±49.6)	2.10 b
Fertigation	6660.4 (±341.2)	1.92 (±0.05)	117.5 (±7.5)	206.4 (±17.1)	2.03 b
p [1]	ns	ns	ns	ns	0.000
			Maize		
Reference	6021.6 (±205.3) a	1.35 (±0.07)	74.4 (±2.7) a	143.3 (±8.6)	0.50 a
Open Discs	6505.4 (±340.2) a	1.39 (±0.01)	82.3 (±2.9) ab	160.0 (±4.1)	0.60 ab
Acidification	7387.9 (±283.5) b	1.36 (±0.02)	92.2 (±4.6) b	159.5 (±5.8)	0.71 b
Fertigation	6707.3 (±345.2) ab	1.39 (±0.01)	85.2 (±4.1) ab	161.7 (±4.4)	1.14 c
p [1]	0.046	ns	0.037	ns	0.006

[1] ANOVA; Probability of an effect of application system, ns: not significant ($p > 0.05$). Values in the same column followed by the same letter are not significantly different ($p > 0.05$) (Tukey test).

Nitrogen use efficiency was higher in the acidification and fertigation systems than in the reference because of the lower N rates applied with these two methods.

The postharvest mineral nitrogen content (0–30 cm) was slightly higher in the pivot plot than in the other three plots (Table 4). However, the application system did not significantly affect the mineral nitrogen content in the soil profile (0–90 cm) after maize harvest, although the lowest numerical value was observed under fertigation.

Table 4. Soil mineral N content (Nmin) under the different application methods: at wheat harvest (0–30 cm, 4 July 2022) and at maize harvest (0–90 cm, 14 November 2022).

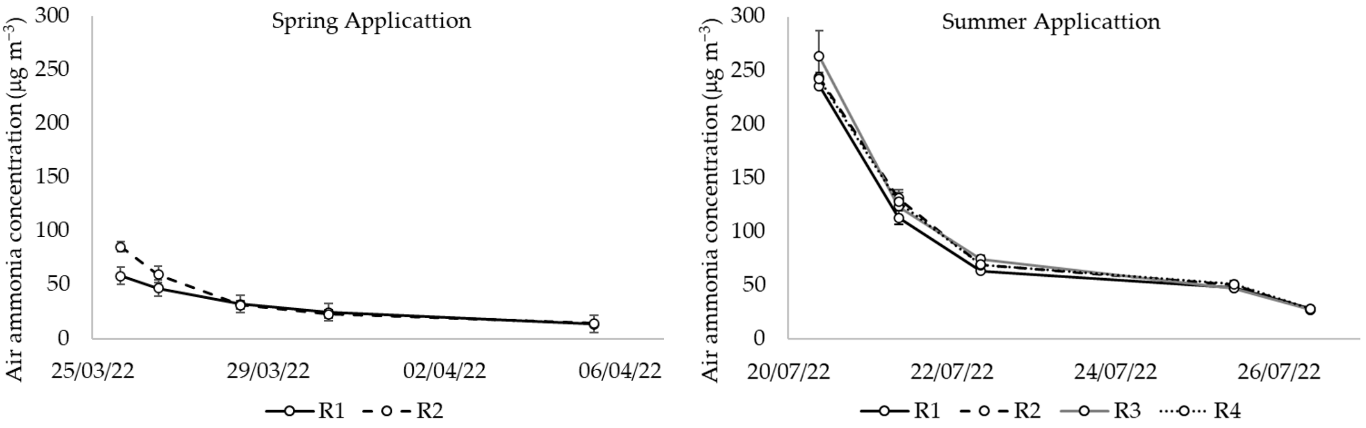
	Nmin (0–30 cm) 4 July 2022 (kg N ha−^{1})	**Nmin (0–90 cm) 14 November 2022 (kg N ha−^{1})**
Reference	26.5 a	96.4
Open Discs	22.8 a	103.8
Acidification	18.6 a	165.1
Fertigation	43.7 b	65.6
p [1]	0.0005	ns

[1] ANOVA; Probability of an effect of application system, ns: not significant ($p > 0.05$). Values in the same column followed by the same letter are not significantly different ($p > 0.05$) (Tukey test).

3.3. Ammonia Emissions

The ammonia air concentration measured at the masts within the plots peaked the first day after digestate application. In all the cases, the ammonia air concentration sharply decreased after the day of application, as shown in Figure 2, for the reference plots.

For spring topdressing, acidification and fertigation reduced ammonia emissions relative to reference, while disc injection had no significant effect (Table 5). The most efficient system for emission reduction was acidification, with a 79% reduction, followed by fertigation, with a 54% reduction. For summer digestate fertilization, acidification remained the most effective, reducing emissions by 92%, and disc injection achieved a 76% reduction, showing greater efficiency than in the spring topdressing application (Table 6).



(**a**) (**b**)

Figure 2. Air ammonia concentration measured in the reference plot after digestate application (**a**) in spring in the two monitoring stations (R1, R2) deployed within the plot and (**b**) in summer in the four monitoring stations (R1, R2, R3, R4) deployed within the plot. Vertical bars represent the standard error.

Table 5. Ammonia emissions from digestate spring topdressing to wheat for the different application techniques. Total Kjeldahl nitrogen (TKN, kg N ha^{-1}) applied, total ammonium N (TAN, kg N ha^{-1}) applied, ammonia emissions (% of TKN and % of TAN applied), and emission reduction relative to the reference system (% of TAN).

	TKN	**TAN**	**NH_3–N Emissions**			**Reduction vs. Reference** [1]
	(kg N ha^{-1})	**(kg N ha^{-1})**	**(kg N ha^{-1})** [2]	**% TKN**	**% TAN** [2]	**%**
Reference	199.0	96.0	13.7 a	6.9%	14.3% a	-
Open Discs	198.8	99.4	8.4 ab	4.2%	8.5% ab	40.5%
Acidification	97.7	64.2	1.9 b	1.9%	2.9% b	79.4%
Fertigation	101.7	76.3	5.0 b	4.9%	6.6% b	53.8%

[1] Reduction over the %TAN applied. [2] Values in the same column followed by the same letter are not significantly different ($p > 0.05$), (Tukey test).

Table 6. Ammonia emissions from digestate summer basal application for the different application systems. Total Kjeldahl nitrogen (TKN, kg N ha^{-1}) applied, total ammoniacal N (TAN, kg N ha^{-1}) applied, ammonia emissions (% of TKN and % of TAN applied), and emission reduction relative to the reference system (% of TKN).

	N Total	**NH_4^+–N Rate**	**NH_3–N Emissions**			**Reduction vs. Reference** [1]
	(kg N ha^{-1})	**(kg N ha^{-1})**	**(kg N ha^{-1})** [2]	**% N Total**	**% TAN** [2]	**%**
Reference	126.1	87.4	26.4 a	20.9%	30.2% a	-
Open Discs	105.4	80.4	5.8 b	5.5%	7.2% b	76.2%
Acidification	63.5	56.9	1.4 b	2.1%	2.4% b	92.1%

[1] Reduction over the %TAN applied. [2] Values in the same column followed by the same letter are not significantly different ($p > 0.05$), (Tukey test).

Ammonia emissions after the urea topdressing application to maize differed significantly between the reference plot (7.3 kg N ha^{-1}) and the AC + D plot (21.4 kg N ha^{-1}). Measurements from the two background masts surrounding the reference plot were unexpectedly high, nearly matching values recorded in some masts within the plot (Figure S4), suggesting external contamination. Due to this suspected contamination, the emissions estimated for the reference plot were disregarded, and emission from AC + D plot was used as a proxy for the reference plot (Table 7). Ammonia emissions for the whole maize cycle were calculated by adding the emissions estimated after basal and side-dressing fertilization.

Table 7. Ammonia emissions from digestate basal application and urea side-dressing application to maize with different application systems. Total nitrogen applied with digestate and urea (N total), ammonia emissions of basal and side-dressing applications, total emissions and percentages of the TAN applied (%TAN), and emission reductions relative to the reference system (% TAN).

	N Total (kg N ha^{-1})		**NH_3–N Emission**				**Reduction vs. Reference** [1]
	Basal	**Side Dressing**	**Basal kg N ha^{-1}**	**Side Dressing (kg N ha^{-1})**	**Total (kg N ha^{-1})**	**% TAN** [2]	**%**
Reference	126.1	160	26.4	21.4	47.7	19.3% a	-
Open Discs	105.4	160	5.8	21.4	27.1	11.2% b	41.5%
Acidification	63.5	160	1.4	21.4	22.7	10.5% b	45.7%
Fertigation	-	142	-	5.5	5.5	4.7% c	75.9%

[1] Reduction over the %TAN applied. [2] Values in the same column followed by the same letter are not significantly different ($p > 0.05$), (Tukey test).

Considering basal and side-dressing fertilization in the summer crop, the reduction in ammonia emissions achieved by acidification and disc injection was lower than that achieved in the digestate basal application, since the majority of emissions occurred after the application of urea. Acidification was slightly more effective at reducing emissions (45.7%) than disc injection (41.5%). The application of digestate via fertigation, entirely as side-dressing, was particularly noteworthy, as it could reduce ammonia emissions by 75.9% under the experimental conditions (Table 7).

4. Discussion

4.1. Crop Response

Wheat yield and N extraction were not affected by the application system. The average wheat yield of all the application systems (5729 kg ha^{-1}) was similar to that of other experiments in the same area; Yagüe and Quílez [3] reported wheat yields ranging from 5000 kg ha^{-1} to 5100 kg ha^{-1}, and Mateo-Marín et al. [46] reported yields between 5491 kg ha^{-1} and 8357 kg ha^{-1} in irrigated wheat field experiments that involved fertilization with pig slurry. The statistical information of the Ministry of Agriculture, Fisheries and Food [47] shows yields ranging from 4836 to 5903 kg ha^{-1} for irrigated wheat. The maize yield was significantly greater under acidification (7387.9 kg ha^{-1}) than under the reference treatment (6021.6 kg ha^{-1}), although no differences were detected in N uptake among the two systems. The average yield, 6656 kg ha^{-1}, was lower than typical second-crop yields in the region [48,49] due to maize sowing being performed very late. Increased yields with acidification were observed in some crops because of the increased availability of nutrients [27].

The topsoil (0–30 cm) was slightly saline in the adjacent disc, acidification and pivot plots ($EC_{1:5}$ = 0.22–0.26), whereas in the reference plot, the topsoil was moderately saline ($EC_{1:5}$ = 0.64) (Table S4) and could have affected yield in this plot. Wheat and maize yields were the lowest in this plot, although no significant differences were found except between the disc and acidification systems for maize.

Nitrogen use efficiency (NUE) reflects the effectiveness of fertilizer management: values between 0.5 and 0.9 indicate efficient use; values below 0.5 suggest inefficiency, with potential soil nitrogen surpluses and contamination risks; and values above 0.9 indicate soil nutrient mining, which may cause long-term soil degradation [50]. In wheat, the reference and disc systems, where the N rate matched crop requirements, achieved an NUE of 0.84, indicating efficient fertilizer management (Table 2). In contrast, acidification and fertigation showed NUE values above 2, as the applied doses (105 and 102 kg N ha^{-1}, respectively) were far below crop needs, indicating nitrogen mining from soil reserves. In maize, NUE ranged from 0.50 to 0.71 in all systems except fertigation, where it exceeded 1, indicating soil nitrogen mining. In fertigation, the total N supply was much lower than that in the other 3 systems (Table 7) because of N fractionation. Nitrogen splitting prevents soil N accumulation and associated losses (nitrate leaching and N_2O and ammonia emissions), allowing for reduced N application rates. Thus, Herrero et al. [34] also reported that, using pig slurry fertigation with pivot and drip systems, N application rates could be reduced compared with traditional methods, without jeopardizing crop yield. However, in this study the low N rates applied under fertigation are not sustainable in the long term, requiring adjustment to prevent soil degradation. After the experimental period, the mineral nitrogen content in the soil profile under fertigation did not differ significantly from that in the other systems (Table 3), although it was slightly lower numerically.

4.2. Ammonia Emissions

Ammonia emissions were estimated using the bLS method, with ammonia air concentrations obtained from passive ALPHA® samplers. Kamp et al. [36] analyzed the errors associated with different ammonia emission estimation methods and reported that, in the case of micrometeorological methods, errors may range from 24% to 31% when systematic errors are included. Despite these potential uncertainties, bLS method with Alpha samplers was considered appropriate for achieving the objective of this study, which is to comparatively evaluate the potential of different application techniques to reduce ammonia emissions. Open-path ammonia laser analyzers (GasFinder3, Boreal, Edmonton, AB, Canada) were also deployed to measure ammonia concentrations to obtain short-term emission estimates and to support the data provided by the ALPHA samplers. However, logistical constraints prevented this comparison.

The ammonia air concentrations at the masts within the plots were high during the first three days after digestate application, when declined to background levels. It is well known that ammonia emissions peak in the hours immediately following slurry application, with most emissions occurring within the first 2–3 days [20,36–38].

Ammonia concentration, and, consequently, ammonia emission, was lower in spring following topdressing application to wheat than in summer after basal application in maize. For example, in the reference system, the ammonia concentration ranged between 60 and 80 mg $N–NH_3$ m^{-3} in spring and between 236 and 260 mg $N-NH_3$ m^{-3} in summer on the first day after application (Figure 2). Ammonia emission using trail hoses (reference) was 14.3% of TAN applied in spring topdressing and 30.2% in summer basal application. This difference was associated with two factors: lower spring temperatures (average $\approx$ 13 °C; Figure 1) compared with summer (average $\approx$ 25 °C; Figure 1) [16] and the enhanced soil coverage by the wheat canopy at spring topdressing relative to bare soil during summer basal application [51].

Digestate acidification was the most efficient technique at reducing ammonia emissions, with a 79% reduction in the spring topdressing application (2.9% of TAN applied versus 14.3% of TAN in the reference system) and 92.1% in the summer basal application (2.4% of TAN versus 30.2% of TAN in the reference system). It is important to consider that the N doses applied in acidification were half those applied in the reference system, and it was observed that the digestate infiltrated the soil more rapidly than in the reference, where the digestate flooded the whole soil surface. Therefore, the reduction in emissions was attributable not only to acidification but also to the lower coverage of the soil surface with slurry [31], even when relative emissions were considered.

Acidification has been documented as a very efficient ammonia emission mitigation strategy for slurries. Many works have evaluated ammonia emission abatement in land application of slurry (mainly cattle slurry) with acidification under different conditions. Bussink et al. [52] reported that in different soil types in the Netherlands, ammonia emissions decreased between 85% and 55% with the acidification of cattle slurry (pH between 4.5 and 6, respectively) under broadcast application. Nyameasem et al. [37] reported a consistent reduction in NH_3 emissions with cattle slurry acidification (pH = 6) at four sites in Germany, ranging from 42% to 77% depending on site and year. Fangueiro et al. [28] and Keskinen et al. [25] reported that acidification reduced ammonia emissions significantly, even more than soil injection did, as was observed in this work. Additionally, acidification (pH = 5.5) reduced ammonia emissions in separated cattle slurry liquid fractions [22,28,53], pig slurry liquid fractions [53], and digested cattle slurry [22]. Slurry acidification in those studies resulted in a significant reduction in ammonia emissions (between 42% and 97%) that was comparable to that measured in this work (between 72 and 92%). Most of those works reduced the pH after acidification to 5.5 or even lower. The potential of acidification to reduce ammonia emissions depended on the pH of the applied slurry, with the potential increasing as the pH decreased [23,54]. In this study, acidification decreased the digestate pH to values between 6.5 and 6.9 (Table S1), and at that level, acidification very efficiently reduced ammonia emissions from the digestate. Simulations in the ALFAM2 model have shown that a pH of 6.6 is the average target for acidified pig and cattle slurries to achieve a 25% reduction in ammonia emission [55]. In this experiment, with a pH of 6.5–6.9, acidification resulted in relatively high abatement potential, partially because of the lower rates of digestate applied in comparison to reference application, which favoured its infiltration into the soil.

Injection of slurry into the soil is considered a very efficient mitigation practice for ammonia losses after field application [56,57]. However, studies evaluating the efficiency of open-slot injection relative to band application are fewer than those on acidification and, in some cases, report contradictory findings. In our study open disc injection moderately reduced ammonia emissions but was not as efficient as acidification. In spring topdressing application emissions were reduced by 40.5%, although the reduction was not statistically significant in relation to band application while in summer the emission reduction was greater and significant, reaching 76.2%. These results are in agreement with the work of Nyameasem et al. [37], which, when working with cattle slurry at four sites in Germany, observed a consistent reduction in NH_3 emissions (45.7 ± 7) with acidification (pH = 6), whereas the reduction with slurry injection was lower (21.2 ± 6.2) and inconsistent; in some cases, the injection technique even increased ammonia losses. Similarly, Keskinen et al. [25] found that ammonia volatilization was reduced more effectively by acidification (90–97%) than by injection (35–64%), with emissions under injection not differing significantly from those of band application.

It has to be highlighted that in our study during spring topdressing application the soil was very humid because of prior rainfall, which prevented the equipment from injecting the digestate properly in some areas. This led to slurry surplus in the open slots, exposing slurry to the atmosphere and thereby increasing emissions [29]. This limitation represents a drawback of the open disk injection system. In this sense, closed-disc injection, which was not evaluated in this study, may reduce ammonia emissions more effectively than open-slot injection [58].

Fertigation is considered a technique for reducing ammonia emissions in the Guidance from the UNECE Task Force on Reactive Nitrogen [59]. The reduction in ammonia emissions indicated by this method is proportional to dry matter dilution, with a 50% dilution level resulting in a 30% reduction in emissions. Concurrent factors, in addition to dilution, contribute to the mitigation of ammonia emissions with fertigation. First, the digestate needs to be filtered before it can be injected into the irrigation system to avoid clogging the nozzles of drippers or sprinklers; the liquid fraction obtained after the separation process has a dry matter content that is lower than that of the raw digestate [60–62], and it consequently has a lower emission potential [38]. Second, the soil is protected by the crop canopy as fertigation is applied when the crop partially or completely covers the soil surface, differing from basal application directly over the soil [51]. Third, fertigation could reduce the total amount of N applied because of N splitting [34]; consequently, ammonia emissions are reduced. Finally, the low TS content of the liquid fraction increases the infiltration rate into the soil and can decrease emissions [63].

Some studies have analysed the effects of fertigation with slurries, but most of them have focused on the responses of crops [64,65], the risk of nitrate leaching [66–68] and the effect on greenhouse gas emissions [64]. Only a few works have measured the ammonia mitigation potential of slurry fertigation. In a maize crop, Herrero et al. [34] reported a significant reduction in ammonia emissions (76%) with fertigation in pivot systems with liquid fraction of pig slurry relative to that of a reference system with broadcast slurry application at base dressing supplemented with urea at topdressing. Provolo et al. [69] reported an ammonia emission reduction of 64% in a pivot with digestate incorporation at base dressing and fertigation with digestate liquid fraction at side-dressing in comparison to a reference plot with digestate incorporation at base dressing. The reduction in ammonia emissions observed in this study for maize fertigation (75.9% in summer) is consistent with the reductions reported in those two studies, although differences in the reference plots should be considered: broadcast application in [34] and broadcast with incorporation in [69] versus band application in this work.

Fertigation was highly efficient at reducing ammonia emissions in summer application, although in spring it did not reach the levels achieved by acidification. Thus, for summer crop fertilization, fertigation was the most effective system for abating ammonia emissions, achieving a reduction of 75.9% relative to the reference. Even though acidification could reduce ammonia emissions by 92% during summer basal applications, emissions from the application of urea topdressing partially offset this reduction.

It should be noted that other factors may increase ammonia emissions in the fertigation technique, such as the losses produced during the separation process, although some researchers have considered these emissions low [70]. Additionally, some works have shown that at the storage level, the digestate liquid fraction emits more ammonia than the digestate does [70,71], likely due to its lower total solid (TS) content, which hinders the formation of a surface crust that limits volatilization [61].

4.3. Advantages and Limitations of the Application Systems

Although the results presented are quantitatively specific to a single-year experiment under specific agrometeorological conditions and therefore cannot be generalized, they are qualitatively valuable for assessing the capacities of different application systems to reduce ammonia emissions to the atmosphere in Mediterranean areas. In this context, Table 8 provides a summary of the advantages and limitations of each application system evaluated in this work.

Table 8. Advantages and limitations of the application systems evaluated.

Method	Advantages	Limitations
Acidification	The most efficient in reducing digestate emissions in spring topdressing and summer basal application	Difficulty in acidifying during application. Complex acidification handling. Custom application equipment requiring high investment.
Disc Injection	Efficient in reducing ammonia emissions both in spring topdressing and summer basal application	Requires more mechanical traction than trailing hose application. Difficult to apply on wet or stony soils.
Fertigation	Highly efficient in reducing emissions from fertilization more important in summer crops. It is very simple if fields are located near a farm/anaerobic digestion facility. Increases nitrogen use efficiency and allows for a reduction in N dose.	Requires separation of slurry and investment in both a separator and injection pump. Difficulty applying in spring if it is rainy.

Acidification has been evaluated as the most effective strategy for reducing ammonia emissions in spring topdressing applications to winter cereals and in summer basal applications. However, in summer crops, if mineral side-dressing is included, the abatement potential is reduced because of the significant contribution of topdressing urea to ammonia emissions. Urea and other ammoniacal fertilizers are commonly used for maize side-dressing; this issue should be addressed by using alternative fertilizers or by splitting the application [14] to avoid counteracting the effect of acidification in the basal application. Some machinery with automated acidification and pH control is commercially available and often used in some North and Central European countries (e.g., Denmark and Germany); however, farmers in Spain have not adopted this technology because of its high cost. Manual acidification of slurry in the spreading tank or prior to application is complex because of the risk associated with the handling of hazardous products and represents a limitation for practical implementation [27].

Open disc injection is efficient at reducing ammonia emissions (40–76%), although it can present problems in stony or wet soils [17], as is the case in this study for wheat application. This system requires additional traction and in general, the working width is narrower than that of trailing hose systems, resulting in higher energy and time consumption [17]. Although this type of equipment is common or even mandatory in some other countries, it is not widely used in Spain and requires significant investment.

Pivot fertigation is highly efficient at reducing ammonia emissions from digestate application, particularly in summer crops (≈76%), where it can replace high-rate basal application. Fertigation allows for lower nitrogen application rates while increasing nitrogen use efficiency (NUE). From an agronomic perspective, fertigation poses certain challenges for continuous application when NUE is > 1, as observed in this study. These challenges should be addressed to enable efficient fertilization management. Fertigation is not applicable to winter crops in areas with high spring rainfall or in unusually rainy years. Fertigation requires the separation of slurry, which involves investment in a separator, liquid fraction storage on the farm, injection pumps, and some maintenance. A preliminary study by Daudén et al. [72] estimated the cost as less than €1.08 per kg of nitrogen in the case of slurry with a nitrogen concentration above 2 kg m^{-3} and a farm-to-field distance reaching 3 km, which is affordable.

5. Conclusions

For summer crops, fertigation is the most effective technique for ammonia abatement compared with traditional fertilization using digestate. Although acidification and injection are also efficient at reducing ammonia emissions during basal applications, the management of topdressing fertilization remains a key factor for effective ammonia mitigation.

For spring topdressing of winter crops, acidification is the most efficient technique for reducing ammonia emissions. However, this method requires a high investment in specialized machinery or, if performed manually, involves complex acid handling. Fertigation is also effective in reducing ammonia emissions, particularly in areas with no humid spring conditions.

In addition to its ammonia abatement potential, fertigation enables a reduction in nitrogen application rates, thereby helping to minimize other system losses (e.g., GHG emissions and nitrate leaching). Although fertigation requires some investment, it is generally cost-effective, especially when fields are located near farms or biogas plants.

Supplementary Materials: The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/agriengineering7100352/s1; Figure S1: Location of the plots on the experimental farm La Melusa; Figure S2: Application of digestate via fertigation with pivot in (top) wheat and (bottom) maize crops, showing one of the ammonia concentration measurement points with the mast and the plate holding the three ALPHA® passive samplers; Figure S3: Filtering ramp and screw separator installed for digestate filtration, with the two containers being used to store (1) the raw digestate and (2) the filtered digestate; Figure S4: Air ammonia concentration after topdressing fertilization to maize in the masts located in (top) the reference and (down) the acidification–disk (AC + D) plots; Table S1: Composition of the digestate applied to wheat and maize with each of the application systems; pH, total solids (TS, % fresh matter), organic matter (OM, % fresh matter), total Kjeldahl nitrogen (TKN) total ammoniacal N (TAN), phosphorous (P_2O_5) and potassium (K_2O); Table S2: Application of digestate liquid fraction (LF) to wheat by fertigation. Date, digestate volume applied (LF–V, m^3), digestate rate (LF–R, m^3 ha^{-1}), dilution ratio (LF:water), and amounts of total Kjeldahl nitrogen (TNK, kg ha^{-1}) and ammoniacal N (TAN, kg ha^{-1}) injected during each fertigation event; Table S3: Application of digestate liquid fraction (LF) to maize by fertigation. Date, digestate volume applied (LF–V, m^3), digestate rate (LF–R, m^3 ha^{-1}), dilution ratio (LF:water) and amounts of total Kjeldahl nitrogen (TNK, kg ha^{-1}) and ammoniacal N (TAN, kg ha^{-1}) injected in each fertigation event; Table S4: Soil characteristics (0–30 cm) in the different plots, pH in the 1:2.5 extract, electrical conductivity in the 1:5 soil extract ($EC_{1:5}$), organic matter (OM), extractable P (Olsen P), extractable K ammonium acetate (K), and texture.

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