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Posted Date: 8 November 2024

doi: 10.20944/preprints202411.0587.v1

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New Insights into Fertilisation with Animal Manures for Annual Double-Cropping Systems in Nitrate Vulnerable Zones of Northeastern Spain

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Abstract: Compared with maize monocropping systems, maize double-cropping production systems have a much greater nitrogen extraction capacity. This study aims to assess if in these farming systems, animal manures could be applied, using adequate management practices, exceeding the maximum annual amount of livestock manure established in the European Nitrate Directive for vulnerable zones (170 kg N ha^{-1}) without increasing the risk of water nitrate contamination. We compare the risk of nitrate leaching under two fertilisation strategies, one with synthetic fertilisers (M) and the second with maximized application of pig slurry (P). The study was conducted in two contrasting soil types, a deep and heavy-textured soil and a shallow and stony soil. Crop yields and N extractions were not affected by the fertilisation strategies. The nitrate concentrations in the soil below the crop root zone were lower in the deep soil than in the shallow soil, where values exceeded 1000 mg L^{-1}. The soil nitrate concentration was not affected by fertilisation strategies at each site. The results show that pig slurry can be applied above the limit of 170 kg N ha^{-1}, in the conditions of the study up to 360 kg N ha^{-1}, without increasing the risk for nitrate leaching.

Keywords: nitrate leaching; pig slurry; double-cropping; Mediterranean area; nitrate vulnerable zones

1. Introduction

In the last fifteen years, farmers in the Ebro River basin in northeastern Spain have made important efforts to modernize irrigated areas, transforming flood irrigation systems into pressurized irrigation systems with greater control of the irrigation water applied. This change has increased crop yields, but it has also driven a change in crop patterns [1], with an increase in the area dedicated to annual double-cropping systems, mainly winter cereals-maize, green pea-maize, or winter cereals-sunflower. These double-cropping systems, although more intensive, are of environmental interest because the soil remains covered throughout the year and can reduce nitrate losses by leaching [2–5]. In a double-cropping rotation, a crop could use the residual mineral N from the previous crop, increasing the nitrogen use efficiency (NUE) of the system and thus reducing the risk of nitrate leaching [6,7]. Similarly, soil cover reduces soil losses due to erosion and the associated losses of nutrients such as phosphorus [8].

Spain, with 38 million pigs, accounts for 25% of the total European pig population [9], and in northeastern Spain, the regions of Aragon (9.6 million head) and Catalunya (8 million head) constitute 52% of the Spanish pig population [10]. The slurry produced is applied as organic fertiliser to crops, but inadequate rates, application methods and management can have negative environmental consequences, such as nitrate leaching [1] or emissions of reactive N to the atmosphere [11,12]. Thus, the nitrogen use efficiency needs to be increased to reduce N losses to the environment, as recommended by the expert panel of the European Union [13]. The design and implementation of the best management practices that optimize the combined use of manures and mineral fertilisers are essential at the local and regional levels to achieve this objective.

Compared with maize monocropping systems, maize double-cropping production systems have a much greater N extraction capacity [2,14–16]. In these farming systems with high extraction rates, animal manures, particularly pig slurries, could be applied to the two crops at adequate rates and under appropriate management practices. Under these premises, the N amounts applied using animal manures will exceed the maximum amount of livestock manure specified in the European Nitrate Directive [17] (EU, 1991) for vulnerable zones (170 kg N ha^{-1} and year), but we hypothesize that this will not increase the risk of water nitrate contamination.

This consideration is based on two aspects: on the one hand, pig slurry replaces mineral fertilisers and reduces the introduction of synthetic N in the system, especially in areas with high livestock density. A reduction in the input of synthetic N in these systems would decrease nutrient surpluses and environmental pollution [18] and increase the efficiency of N use. It is also important to consider that the N fertiliser industry is energy intensive, with high levels of associated greenhouse (GHG) gas emissions. On the other hand, in double-cropping systems, the application of pig slurry to the summer crop is delayed until June–July (depending on the rotation) in comparison to monoculture systems, where slurry is usually applied in April. Nitrate leaching can be significant from April to mid-June before the development of maize roots [19] and is associated with a high probability of rain during that period in northeastern Spain [20]. The delay in slurry application and crop sowing decreases the risk of N washing (from the slurry and from the mineral fertilisers), which is associated with faster crop development in the maize and a reduced probability of rainfall.

A few works have analysed the agronomic efficiency of manure in comparison with that of mineral fertilisation in double-cropping systems using manure rates that exceed the 170 kg N ha^{-1} per year limit established by the EU Nitrate Directive [2,14,21–25] and the information available that compares the nitrate leaching potential between mineral and organic fertilisation in these systems is scarce. Only two of above mentioned studies [2,24] have analysed the risk for nitrate leaching; the results showed that organic fertilisation does not have a greater nitrate leaching potential than mineral fertilisation does. The meta-analysis by Hina [26] also revealed that nitrate leaching losses do not differ between organic fertilisers and synthetic fertilisers, but the limited research on the impact of organic fertilisers on nitrate leaching indicated that more in in-depth studies are necessary to provide data to ensure the sustainability and coexistence of agricultural and farming systems in the future.

Thus, the objective of this work is to compare traditional fertilisation methods with mineral fertilisers versus a fertilisation plan that maximizes pig slurry application to cover crop N needs at appropriate times in double-cropping systems in high-yield Mediterranean areas. The comparison will be carried out in two contrasting soils whose potential risk for nitrate leaching differs. The comparison will focus on crop yield, N uptake and the risk of nitrate leaching.

2. Materials and Methods

2.1. Site and Experimental Design

The experiments were set up in two commercial fields with contrasting soil characteristics. Fields were chosen to represent the characteristics of soils in the irrigated areas of northeastern Spain. The first field (Torremira) represents a “saso” soil (mesa) located on alluvial terraces and characterized by a shallow depth (0.50 m) with a petrocalcic horizon below, sandy clay texture, high stoniness, and low water retention capacity and is thus very prone to nitrate leaching. The second field (Barluenga) represents the deep alluvial soil typical of river valleys. This soil is clay textured, deep (>1.2 m), without stones, has a high water retention capacity and is less prone to nitrate leaching. These fields differ in terms of their irrigation methods: Torremira is sprinkler irrigated (staggered 15 m × 15 m frame), whereas Barluenga is surface irrigated.

The soil characteristics in the two fields at the beginning of the experiment are presented in Table 1. The potassium concentrations (top layer) are high in both soils, whereas the P concentrations are low, especially in the heavily textured Barluenga soil.

Table 1. Soil characteristics, depth, electrical conductivity in the 1:5 soil extract (EC1:5), organic matter (OM), extractable P (P Olsen), extractable K ammonium acetate (K), texture, stoniness (Ston.) and soil mineral N (Nmin) at the beginning of the period in the two experimental fields.

Site and Soil Characteristics	Barluenga				Torremira	
Depth (cm)	0-0.3	0.3-0.6	0.6-0.9	0.9-1.2	0-0.3	0.3-0.5
$EC_{1:5}$ (dS m^{-1})	0.21	0.30	0.53	0.311	0.17	0.18
OM (mg kg^{-1})	24.2	17.2	13.2	11.2	22.7	17.5
P Olsen (mg kg^{-1})	16.3	7.4	7.9	10.3	18.4	7
K (mg kg^{-1})	651.9	444.1	634.2	613.7	418.1	173.7
Sand (mg kg^{-1})	175	175	140	163	537	623
Silt (mg kg^{-1})	200	204	221	220	76	173
Clay (mg kg^{-1})	625	621	639	617	386	204
Ston. (mg kg^{-1})	5.1	8.2	4	0.6	54.8	57.6
Nmin (kg ha^{-1})	61.2	63.2	28.7	14.4	38	18.3

In Torremira, a rotation of green pea–maize (in the last year, green pea was substituted with barley due to commercial factors) was evaluated for three years. Green pea is only cropped in this type of soil to ensure that soil conditions do not constrain the entry of the combine for harvesting. Although green pea does not need N fertilisation, pig slurry is applied to cover its P and K requirements. In Barluenga, a double-cropping wheat–maize was evaluated for 2.5 consecutive years.

Two fertilizers treatments were compared in each of the trials, namely, a treatment with all the nitrogen provided by mineral fertilisers (M) and a manure treatment where fertilisation with pig slurry (P) was maximized. In both cases fertilization rates were adjusted to crop N requirement.

In winter cereals, fertilisation was applied to cover all crop N needs during side dressing, as it is considered that presowing fertilisation has low efficiency [27] and that postponing N application at tillering is a good technique for reducing nitrate leaching. In the maize crop, pig slurry was applied before sowing and complemented with mineral N in the plots corresponding to the P treatment by following the recommendation of Iguacel et al. [28] who reported that in the study area, it was not possible to obtain maximum yields of the second maize crop using only pig slurry at presowing, but the crop required the application of approximately 35% of the N rate as side dressing.

The design was a complete randomized block with 4 replicates. The size of each experimental plot was 15 m × 30 m at Barluenga and 15 m × 45 m at Torremira. Pig slurry was applied by hanging hose machinery by the Tauste Manure Management Center (https://www.taustecge.es/), which is located near the two experimental fields.

The climate of the area is a semiarid Mediterranean continental climate with a mean annual air temperature of 14.3°C, mean annual precipitation of 325.0 mm, and mean annual reference evapotranspiration of 1276 mm (period 2006-2023). The meteorological conditions during the experimental period are presented in Figure S1.

doi:10.20944/preprints202411.0587.v1

2.2. Agricultural Practices

2.2.1. Barluenga Site

Durum wheat (*Triticum durum* L. cv. “Calero”) was sown in Barluenga field on 16/11/2016, 19/11/2017 and 16/11/2018, with 300 kg seeds ha^{-1}. The nitrogen rate was set to 120 kg N ha^{-1} for a first top dressing at the tillering stage and was complemented with a second dressing (30 kg N ha^{-1}) at the booting stage to improve grain quality.

For the first side dressing, pig slurry was applied to the plots corresponding to the P treatment, and green N (N-Mg-S:30-0.6-2.6) was applied to the plots corresponding to the M treatment. During late side dressing, mineral fertiliser (green N) was applied to all the plots. Pig slurry was applied to the P plots on 02/03/2017, 03/02/2018, and 01/03/2019, and green N was applied to the M plots on 08/03/2017, 03/02/2018 and 01/03/2019 for the tillering application and on 11/04/2017, 17/03/2018 and 06/04/2019 to all plots for the booting application.

Maize (*Zea maize* L. cv. “Kenovis”) was sown on 16/06/2017 and 03/07/2018 at a density of 110,000 plants ha^{-1}. In the plots corresponding to the P treatment, pig slurry was applied before sowing at a theoretical rate of 170 kg N ha^{-1} and complemented with mineral N at the 4-leaf stage (120 kg N ha^{-1}). In the plots corresponding to the M treatment, mineral N was applied at the 4-leaf stage at a rate of 270 kg N ha^{-1}.

2.2.2. Torremira Site

Green pea (*Pisum sativum* L. cv. “Mastin”) was sown on 01/02/2017 and 12/12/2017 using 220 kg seeds ha^{-1}. Pig slurry was applied at a target rate of 120 kg N ha^{-1} in plots corresponding to the P treatment at presowing (26/01/2017) in 2017 and as side dressing in 2018 (02/02/2018). The target N rate was chosen by considering the average pig slurry N/P_2O_5 ratio in the study area (1/1.6, [29]) to provide 70 kg P_2O_5 ha^{-1}. In the plots corresponding to the M treatment, compound 9-26-15 fertiliser at a rate of 400 kg ha^{-1} was applied in 2017, and 400 kg of superphosphate (18%) was applied in 2018. The barley crop (*Hordeum vulgare* L. cv. “Pewter”) was sown on 12/12/2018, using 300 kg seeds ha^{-1}. At the end of tillering, pig slurry was applied at a target rate of 150 kg N ha^{-1} to the plots corresponding to the P treatment, and green N (150 kg N ha^{-1}) was applied to those corresponding to the M treatment.

Maize (*Zea maize* L. cv. “P0725”, “P0222Y+P0222”, “P1570Y + P1570” for years 2017, 2018 and 2019 respectively) was sown on 18/06/2017, 30/06/2018 and 24/06/2019 at a density of 95,000 plants ha^{-1}. In the plots corresponding to the P treatment, pig slurry was applied before sowing at a theoretical rate of 170 kg N ha^{-1} and was complemented with mineral N at the 4-leaf stage(100-150 kg N ha^{-1}) and at tasselling (60 kg N ha^{-1}, with sprinkler irrigation). In the plots corresponding to the M treatment, mineral N was applied at the 4-leaf stage (240-270 kg N ha^{-1}) and at tasselling (60 kg N ha^{-1}, with sprinkler irrigation). The application of nitrogen at tasselling is typical in the area in sprinkler irrigated fields.

Phosphorous and potassium were applied to the M plots before sowing as needed. The agricultural practices in all the plots (irrigation, ploughing, and pest and weed management) were conducted by farmers following the usual practices in their fields.

The ammonium content of the slurry in the distribution tanks was determined indirectly in the field prior to each application by conductimetry [30] to establish the PS rate to be applied. The total N amounts (kg N/ha) applied to each crop in each year in the two treatments (P and M) in the two experimental plots are shown in Table 2.

The N amounts applied in the plots of P treatments were generally greater than targeted rates, and thus greater than those applied in the M treatments. The differences were generally acceptable except for wheat in Barluenga in 2019 and maize in Torremira in 2018, where the N rates in the P treatment were 54% higher than the target values, and maize in Barluenga in 2017, where the N rate for the P treatment was 40% higher than the target rate (Table 2). On these four occasions, the N total concentration in PS that were estimated in the field from conductimetry were much lower than those measured in the laboratory, resulting in higher-than-expected nitrogen rates (Figure S2). In the green pea in Torremira the amount of phosphorous applied with pig slurry (127 and 87 kg P_2O_5 ha^{-1} in years 2017 and 2018 respectively) also exceeded the target rate. The nutrient concentration of the pig slurry applied to each crop at the two sites is presented in Table S1.

Table 2. Total N amounts (kg N/ha) applied to each crop in each year in the two treatments (P: pig slurry, M: mineral fertiliser) in the two experimental plots (Barluenga and Torremira). PS indicates N supplied with pig slurry.

	Before sowing		**Top-dress 1**		**Top-dress 2**		**Total**
Year-Treatmet-Crop	**N rate Kg N/ha**	**Date**	**N rate Kg N/ha**	**Date**	**N rate Kg N/ha**	**Date**	**N rate Kg N/ha**
				Barluenga			
2017-P-Wheat	36	16/11/16	96 (PS)	02/03/17	30	11/04/17	162
2017-M-Wheat	36	16/11/16	120	08/03/17	30	11/04/17	186
2017-P-Maize	245 (PS)	16/06/17	120	30/06/17	-		365
2017-M-Maize	-	-	270	30/06/17	-		270
2018-P-Wheat	-	-	139 (PS)	03/02/18	30	17/03/18	169
2018-M-Wheat	-	-	120	03/02/18	30	17/03/18	150
2018-P-Maize	165 (PS)	03/07/18	120	22/07/18	-		285
2018-M-Maize	-	-	270	22/07/18	-		270
2019-P-Wheat	-	-	231 (PS)	01/03/19	30	06/04/19	261
2019-M-Wheat	-	-	120	01/03/19	30	06/04/19	150
				Torremira			
2017-P-Pea	261 (PS)	26/01/17					261
2017-M-Pea	36	26/01/17					36
2017-P-Maize	191 (PS)	02/06/17	120	30/06/17	60	14/07/17	371
2017-M-Maize	48	18/06/17	240	30/06/17	60	14/07/17	348
2018-P-Pea		20/12/17	108 (PS)	02/02/18			108
2018-M-Pea		20/12/17					0
2018-P-Maize	262 (PS)	28/06/18	100	18/07/18	60	05/08/18	422
2018-M-Maize		18/06/17	240	18/07/18	60	05/08/18	300
2019-P-Barley			205 (PS)	06/03/19			205
2019-M-Barley			150	06/03/19			150
2019-P-Maize	179 (PS)	24/06/19	150	15/07/19	60	06/08/19	389
2019-M-Maize		24/06/19	270	15/07/19	60	06/08/19	330

2.3. Sampling and Analytical Procedures

2.3.1. Soil Sampling

The soils were sampled at the beginning of the experiment after the maize harvest each year to evaluate the soil mineral N content (Nmin). The soils were sampled using a manual auger at depth intervals of 0.30 m to a depth of 1.20 m in the Barluenga field and at intervals of 0–0.30 m and 0.30–0.50 m in the Torremira field. At least three soil cores were taken from each depth (9 soil cores at 0-0.3 m depth) and combined for further analyses. For the initial sampling, fields were sampled in blocks and the average Nmin value was assigned to the entire experimental filed. A soil subsample was dried (105°C) to determine the soil gravimetric water content. The nitrate and ammonium concentrations were determined in 1:3 soil extracts (10 g of fresh soil:30 mL of 2 N KCl) by colorimetry using a segmented flow analyser (AutoAnalyser 3, Bran+Luebbe, Germany). The soil mineral N contents were calculated as the sum of NO_3-N and NH_4-N considering the soil depth and stoniness.

2.3.2. Nitrate Concentrations of Soil Solution

Ceramic suction cups (Irrometer SSAT, 22 mm Ø, CA, USA) were installed in all plots of each experimental field (8 per plot) to sample the soil solution below the crop root zone. Tubes with ceramic cups at their ends were inserted vertically into the soil, and mud slurry was added to ensure good contact with the soil and to avoid preferential flows along the tube walls (Figure S3). The ceramic cups were installed at depths of 1.20 m in the Barluenga field and at 0.45 m in the Torremira field immediately after the first N application in each crop cycle. The suction cups were removed at harvest for each crop. The soil solution was extracted from the suction cups via a syringe 24 hours after creating a vacuum inside (≈ - 0.7 bars) using a manual pump. The nitrate concentrations in the solution samples were determined in the laboratory by colorimetry using a segmented flow analyser (AutoAnalyzer 3, Bran+Luebbe, Germany).

2.3.3. Crop Sampling

At maturity, the crops were harvested by hand to determine the grain yield, total biomass and nitrogen absorption in the grains and in the remaining aboveground matter.

Wheat, barley, and green pea were harvested from 4 subareas of 0.25 m^2 that were randomly selected in each experimental plot. In Barluenga, wheat was harvested on 15/06/2017, 30/06/2018 and 20/06/2019, and in Torremira, green pea was harvested by hand on 26/05/2017 and 25/06/2018, and barley was harvested on 24/06/2019.

In the case of maize, 3m length strips were selected randomly in two different lines, in those strips all cobs were collected, and the rest of the plants were weighed. The humidity of two randomly selected plants was determined by oven drying at 65°C. Cobs were shelled to obtain the grain yield and humidity. Maize was harvested on 30/10/2017 and 15/11/2018 in Barluenga and on 23/11/2017, 29/11/2018 and 02/12/2019 in Torremira.

The grain humidity was measured (Grain moisture PM-600, Kett, Tokyo, Japan), and the yield was reported on the basis of a moisture content of 120 g kg^{-1} for wheat and barley and 140 g kg^{-1} for green pea and maize. The nitrogen concentrations in wheat grains and straw, pea grains, maize grains and the remaining aboveground biomass were analysed by dry combustion (TruSpec CN, LECO, St. Joseph, MI, USA) in samples that were previously oven dried at 65°. The nitrogen use efficiency (NUE) was calculated as the ratio between the N content in the aboveground biomass of the crop and the amount of N applied. The NUEs were calculated for each crop and year and for the entire rotation at each site.

2.4. Data and Statistical Analysis

The data were subjected to analysis of variance, and the differences among treatment means were determined with Tukey's test. Repeated measures analysis of variance was performed to compare the soil solution nitrate concentrations for each crop season and for the whole data period. On some dates, it was not possible to obtain samples from all the suction cups in each field. For the statistical analysis, only those dates with for 3 or more points for each treatment were considered. The repeated measured analyses of variance required complete data, so missing data were interpolated from the preceding and subsequent sampling dates, and in the case that some of this data was also missing, the average value for the treatment was used.

The soil solution nitrate concentration data was not normally distributed and was log-transformed prior to analysis to ensure data normality. The average nitrate concentration during each period was calculated using the value of the arithmetic mean. Mean estimators for log-normal distributions, such as the Aitchison-Brown estimator or the Finney-Sichel estimator [31,32] (Addiscott 1996; Parkin et al., 1988), were not considered, as nitrate concentrations were used to detect the possible effects of treatments on nitrate leaching but were not intended to quantify nitrate leaching. In all analyses, a significance level of 0.05 was considered. Statistical analyses were performed using the Statgraphics Centurion version 18.1.10 package (Statgraphics Technologies, Inc., The Plains, VA, USA).

3. Results

3.1. Yield and N Absorption

The maize yields did not differ significantly between the P and M treatments or between the two sites and presented some variability between years due to the specific weather conditions in each year. Thus, the average maize yields of the two sites were greater in 2017 (10,812 kg ha^{-1}) than in 2019 (9,273 kg ha^{-1}) (Table S2). In the case of winter crops, no significant differences were observed in wheat (Barluenga) and green pea (Torremira) yields between treatments. Significant differences were observed between the three years for the wheat crop in Barluenga, with the maximum yield occurring in 2019 (Table S3), although no significant differences were observed for the green pea yields in Torremira between 2017 and 2018 (Table S4).

The grain yields and N uptake did not differ between the P and M treatments at any of the two sites for any of the crops within each year (Tables 3 and 4).

The nitrogen use efficiency for the entire period did not differ significantly between the two sites (0.81 kg N kg^{-1} N applied and 0.90 kg N kg^{-1} N applied at Barluenga and Torremira, respectively). No differences in NUE for the entire experimental period were observed between the P and M treatments at either site, Barluenga or Torremira (Table S5). However, differences in the NUE between the two treatments were observed for some crops at Barluenga. Thus, the NUEs were greater under the M treatment than under the P treatment for maize in 2017 and for barley in 2019 (Table S5).

Table 3. Barluenga: Grain yields and crop N extraction of wheat and maize in the two treatments (P: pig slurry, M: mineral fertiliser).

Treatment	Year	Wheat		Maize	
		Grain Yield Kg/ha, 12%	N uptake Kg N/ha	Grain Yield Kg/ha, 14%	N uptake Kg N/ha
P	2017	5078	195	9739	219
M	2017	4771	195	9652	217
p[1]		*ns*	*ns*	*ns*	*ns*
P	2018	6051	172	8364	148
M	2018	5373	148	8781	156
p[1]		*ns*	*ns*	*ns*	*ns*
P	2019	7210	188	-	-
M	2019	7275	192	-	-
p[1]		*ns*	*ns*		

[1] Probability level of the treatment effect after ANOVA. ns: not significant, p > 0.05.

Table 4. Torremira: Yields and crop N extraction of green pea, barley and maize in the two treatments (P: pig slurry, M: mineral fertiliser).

Treatment	**Year**	Green pea (barley in 2019)		Maize	
		Grain Yield Kg/ha, 12%	N uptake Kg N/ha	Grain Yield Kg/ha, 14%	N uptake Kg N/ha
P	2017	6434	-	17663	245
M	2017	6621	-	18033	245
p[1]		*ns*		*ns*	*ns*
P	2018	5535	271	12059	209
M	2018	6329	275	12292	173
p[1]		*ns*	*ns*	*ns*	*ns*
P	2019	8718	187	13337	207
M	2019	8402	153	12230	176
p[1]		*ns*	*ns*	*ns*	*ns*

[1] Probability level of the treatment effect after ANOVA. ns: not significant, p > 0.05.

3.2. Soil Mineral N

The soil mineral nitrogen content (Nmin) at the beginning of the experimental period was high in the Barluenga plot (150.1 kg N ha^{-1}) and lower in the Torremira plot (62.6 kg N ha^{-1}). The average mineral N in the soil at the end of the experimental period never exceeded the initial values at each site (Table 5). The analysis of variance did not detect any differences in soil Nmin content between the M and P treatments in each field at any of the sampling times.

3.3. Soil Solution Nitrate Concentration

The average daily nitrate concentrations of the soil solutions ranged between 0 and 65 mg L^{-1} in the Barluenga field, whereas in the Torremira field, the nitrate concentrations peaked at values higher than 1000 mg L^{-1} on some occasions (Figure 1). The peaks in nitrate concentrations were found in both the P and M treatments. The highest daily nitrate concentration was observed for maize in 2017 at Torremira, where the peak exceeded 2000 mg L^{-1} in the M treatment. The soil nitrate concentrations showed a seasonal pattern in the two treatments; the highest values were observed at the beginning of the crop season after fertiliser application for the four crops, wheat, green pea, barley and maize; then, the values decreased as the crop started to grow and absorb N, while the lowest values were generally observed at harvest (Figure 1).

Table 5. Soil mineral nitrogen (NO_3 + NH_4, kg N ha^{-1}) in the soil profile in Barluenga (0–1.20 m) and Torremira (0–0.5 m) fields at the beginning of the experiment (January 2017) and the maize harvest (December of each year) for the two treatments (P: pig slurry; M: mineral fertiliser). In the Barluenga field, information for the end of the experimental period (07/2019) is also presented.

Site	Treatment	01/2017	12/2017	12/2018	07/2019	12/2019
Barluenga	P	150.1	71.5	111.9	64.9	-
	M	150.1	74.7	133.6	58.0	-
	p[1]	-	*ns*	*ns*	*ns*	
Torremira	P	62.6	65.6	51.9	-	35.0
	M	62.6	68.2	41.6	-	22.6
	p[1]	-	*ns*	*ns*		*ns*

[1] Probability level of the treatment effect after ANOVA. ns: not significant, p > 0.05.

The repeated measures analyses of variance did not detect significant differences between the P and M treatments for each crop or season at either of the two sites. Furthermore, no significant differences were found between the two treatments for the entire experimental period (Table 6). The average nitrate concentration for the crop season was significantly greater at Torremira (285.3 mg L^{-1}) than at Barluenga (10.5 mg L^{-1}).

Table 6. Average nitrate concentration (mg L-1) of the soil solution in the two treatments (P: pig slurry, M: synthetic fertiliser) for the different crops and years and for the total period in the two experimental plots. N indicates the number of data points (dates) in each period, and p is the probability level of the treatment effect after repeated measures ANOVA.

Site	Treatment	2017		2018		2019		Total Period
Barluenga	Crop:	Wheat	Maize	Wheat	Maize	Wheat		
	P	14.3	5.1	3.3	1.3	24.3	-	10.4
	M	31.7	19.6	1.6	5.0	7.6	-	10.7
	N (dates)	2	7	4	8	10	-	31
	p[1]	*ns*	*ns*	*ns*	*ns*	*ns*		*ns*
Torremira	Crop:	Green pea	Maize	Green pea	Maize	Barley	Maize	
	P	353.3	432.8	164.6	437.1	105.6	170.8	274.8
	M	566.3	858.3	71.9	207.0	60.4	113.0	295.8
	N (dates)	2	10	6	9	7	13	47
	p[1]	*ns*	*ns*	*ns*	*ns*	*ns*	*ns*	*ns*

[1] Probability level of the treatment effect after ANOVA. ns: not significant, p > 0.05.

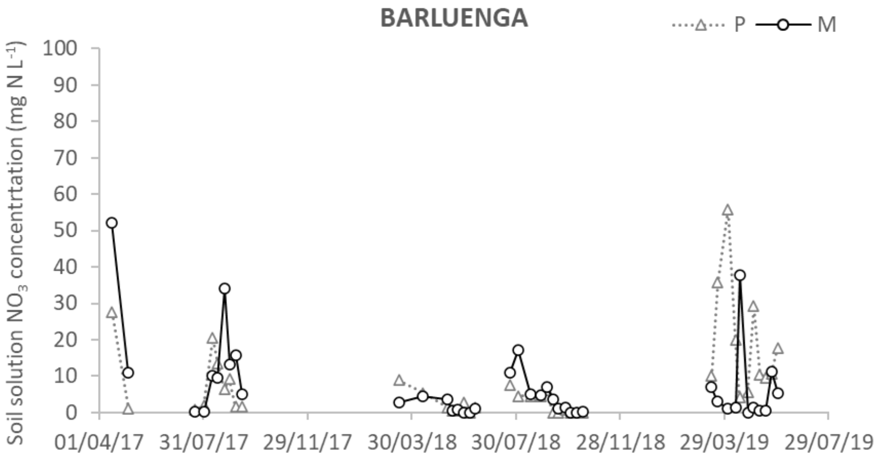
4. Discussion

4.1. Crop Yield and Nitrogen Use Efficiency

The N amounts that were applied using pig slurry to the plots of the P treatments exceeded the target rates by more than 15% in seven of the fifteen applications. In some cases, incorrect estimations of the N contents of the PS occurred, and in other cases, the actual PS rates applied to the field were imprecise. These two factors are key disadvantages for fertilisation with PS and, in general, apply to organic fertilisers in comparison to synthetic fertilisers. The nitrogen content of synthetic fertilisers is well known, and the application machinery is easier to adjust. Although the machinery for PS applications is usually calibrated, applying the appropriate PS rates is difficult, as noted by Daudén and Quílez [33].

Conductimetry was used in the field to estimate the pig slurry N content before application [30], but in some cases, the in situ estimated values of the pig slurry N total concentrations were more than 40% lower than those measured in the laboratory; thus, the N rates applied on those occasions were much higher than the target values (Figure S2). This was the case at Torremira for green pea in 2017 (2.8 versus 4.36 kg m^{-3}), at Barluenga for maize in 2017 (3.0 versus 4.45 kg m^{-3}), maize at Torremira in 2018 (2.6 versus 3.79 kg m^{-3}) and wheat at Barluenga in 2019 (2.7 versus 4.20 kg m^{-3}). The discrepancy in N rates between the two treatments generates an additional source of variability in the comparison of the two treatments.

The yields for the two treatments at the two sites were within the variability range observed in the area for optimal fertilised crops. Yagüe et al. [21] reported yields ranging between 4861 kg ha^{-1} and 7417 kg ha^{-1} for barley and between 7629 kg ha^{-1} and 14248 kg ha^{-1} for maize in a five-year barley–maize rotation. Additionally, Yagüe and Quilez [20] reported wheat yields ranging from 5000 kg ha^{-1} to 5100 kg ha^{-1} in a 1-year irrigated wheat experiment that involved fertilisation with pig slurry, and Mateo-Marín et al. [34] reported yields ranging between 5491 kg ha^{-1} and 8357 kg ha^{-1} in a three-year irrigated wheat field experiment that also involved fertilisation with pig slurry. Moreover, the statistical information from the Ministry of Agriculture [35] shows average yields in the area ranging from 4836-5903 kg ha^{-1} for irrigated wheat, 6241-6290 kg ha^{-1} for green peas and 4558-5507 kg ha^{-1} for irrigated barley. No significant differences in crop yield were detected between the P and M treatments for any site or year, indicating that there were no differences in the response to N fertilisation.



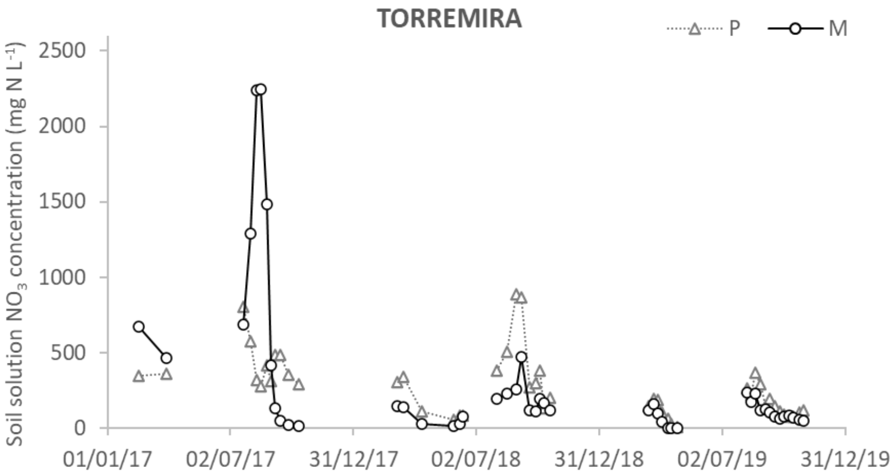


Figure 1. Average nitrate concentration in the soil solution at the different sampling times in the two treatments (P: pig slurry, M: synthetic fertiliser) in the Barluenga (1.2 m depth) and Torremira (0.45 m depth) fields.

The nitrogen use efficiency ranged between 0.52 and 1.28 kg N kg^{-1} N applied (excluding green pea) and was generally in the average range of the possible reference values (between 0.5 and 0.9) defined by the EU Nitrogen Panel [13]. Considering the whole period, the NUEs did not differ between the two sites. The soil at Barluenga has a clay texture, is deep and is supposed to have better nitrogen recovery than Torremira soil, which is shallow. Mateo-Marín et al. [36] in a maize-maize-wheat rotation, reported higher NUEs in a deep soil (1.25m) versus a shallow soil (0.5m) in the same area. However, the rotation in Torremira includes a leguminous crop, and it is well known that leguminous increase the NUE of the systems: the increase is associated with a reduction in the N fertiliser requirement and a low C:N ratio of their residues, which can hasten the mineralization of soil organic nitrogen [37].

For the complete crop rotation, the NUE did not differ significantly between the P and M treatments at either site (Table S5). The differences in NUE between the P and M treatments for specific crops were generally related to the differences in the rates of N applied. Thus, at Barluenga for maize in 2017 and for wheat in 2019, Nue was higher in the P than in the M treatment as the N amounts applied in the P treatment were 35% and 74%, respectively, greater than those applied in the M treatment. Owing to its definition, the NUE clearly decreases as the amount of applied N increases [13].

4.2. Risk for Nitrate Leaching

Measuring N leaching from agricultural fields is complex, as it requires measuring or estimating the volume of water flowing below the crop root zone and its nitrate concentration [38,39]. In this work, we assumed that the amount of drainage volume was equal for the two treatments (P and M) for each crop at each site, as they had the same management, they received the same amount of water by irrigation and precipitation, and no differences in crop evapotranspiration were suspected, as no differences in yield were observed. Under this premise, the nitrate concentration in the solution that drains below the crop root zone is considered a good parameter to compare the risk of nitrate leaching between the two treatments. Different methods are available to measure nitrate concentration in drainage water [39,40]. In this work, we used ceramic suction cups that were installed just below the crop root zone. Ceramic suction cups are not expensive, are easy to sample, and their installation is not troublesome; however, ensuring good contact between the ceramic cup and the soil at the bottom of the hole and the absence of preferential flows along the tube walls is essential [41]. Some studies have shown large variations in nitrate concentrations in soil water extracted from suction cups [42,43]. In general, these studies indicate that suction cups are not adequate in heterogeneous soils or in those that show preferential flow patterns. However, suction cups work well in fairly homogeneous soils [41,43–45] and have been used extensively to estimate nitrate concentrations and nitrate leaching in different systems [7,38,43,46,47].

The soil solution was extracted using a suction of 0.7 bars, so only water from the larger pores was sampled. Thus, the nitrate concentration in the extracted sample did not accurately represent the actual nitrate concentration of the soil solution, as the water in the smaller pores was not sampled. However, water percolation mainly occurs at high soil water contents. When the soil water content decreases, the soil hydraulic conductivity decreases, and water moves more slowly [48]; thus, water draining at high soil tension (in the smaller pores) has a low contribution to total percolation. Therefore, the nitrate concentration of the solution extracted from suction cups is considered a good indicator for comparing the risk for nitrate leching between the two treatments in each field.

The average nitrate concentration of the soil solution for the crop seasons were significantly greater at Torremira than at Barluenga (Table 6). These differences were expected and are related to the soil characteristics. The soil at Barluenga is highly textured with a high clay content and is deep, whereas the soil at Torremira is shallow and with a high stoniness. Soils with high clay content are known to retain water and nutrients more effectively than other soils [49]. Additionally, a meta-analysis of nitrate leaching vulnerability [26] revealed that nitrate leaching losses are expected to be greater from coarse-textured soils than from fine-textured soils. Soil depth also exerts a strong influence on nitrate leaching [50].

The average nitrate concentration during the five crop seasons at Barluenga (between 1.3 and 31.7 mg L^{-1}) were within the ranges observed in drainage water in other experiments that were carried out in drainage lysimeters in the same area. Daudén et al. [51] in an experiment with 0.75-m deep lysimeters (clay loam soil) with maize fertilised with pig slurry, reported nitrate concentrations in drainage water between 5 and 49 mg L^{-1} depending on the treatment, and Salmerón et al. [3], for 1.20-m deep lysimeters cropped to maize with different cover crops and adjusted mineral N fertilisation, reported average nitrate concentrations in the drainage water during the maize crop season between 7 and 44 mg L^{-1}, depending on the cover crop. In lysimeters cropped to maize and wheat at two different depths (1.20 m and 0.50 m) and with the same texture (clay-loam), Mateo-Marín et al. [36] measured nitrate concentrations between 30 and 44 mg L^{-1} in 1.20-m deep soil and slightly higher concentrations, between 54 and 71 mg L^{-1}, in shallow soil (0.50-m deep) in a treatment fertilised with urea. The soil nitrate concentrations in the Torremira field were much higher than those measured in these shallow lysimeters, but the soil texture in the Torremira field is coarser and has a greater proportion of stones that affect the dynamics of water and N in the soil.

Studies in other Mediterranean areas in deep soils using suction cups have reported higher nitrate concentrations in soil solution than those reported in this study for different reasons. Thus, Trindade et al. [46], in northern Portugal in a sandy loam soil in a double-cropping forage system, measured nitrate concentrations in soil solution extracted from suction cups (1 m depth) that were as high as 700 mg L^{-1}, much higher than those measured in the Barluenga field; however, they applied higher rates of nitrogen fertiliser, with an average of 418 kg N ha^{-1} to maize and 194 kg N ha^{-1} to the winter crop. Perego et al. [52], in the Po Valley in deep soils with different textures, obtained 4-year average nitrate concentrations (at depths ranging from 1.3-1.5 m) that ranged from 57 to 243 mg L^{-1} and were related to the soil texture and the amount of N applied (from 309 to 642 kg N ha^{-1} $year^{-1}$). The nitrate concentrations were higher, in both cases, than those reported in this work at Barluenga.

No significant differences in nitrate concentration were detected between the two treatments for the entire experimental period at the two experimental sites, Barluenga and Torremira. Similarly, no significant differences in the average nitrate concentration of the soil solution were detected between the two treatments for each crop season in either of the two sites (Table 6).

In Barluenga, average nitrate concentrations for the wheat and maize seasons ranged between 1 and 32 mg L^{-1} and did not exceed the 50 mg L^{-1} threshold of the EU Nitrate Directive. The average nitrate concentrations for the entire studied period are considered low namely, 10.4 and 10.7 mg L^{-1} for the P and M treatments, respectively. These results indicate that in wheat-maize crop systems in deep soils in the area, mineral nitrogen fertilisation can be substituted completely for pig slurry in the wheat crop and, to some extent (50-70%) in the maize crop, reaching pig slurry rates equivalent to 360 kg N ha^{-1} per year well above the amount of 170 kg N ha^{-1} limit established in the Nitrate Directive, without compromising water quality.

There are only a few works that compare the risk for nitrate leaching of mineral versus organic fertiliser treatments in winter cereal (ryegrass)-maize double-cropping systems. In wheat–maize systems, Du et al. [25] compared the effects on nitrate leaching of digested biogas slurry (DS) injected in the irrigation system at three rates (low, medium and high) versus a conventional mineral fertilisation in a silt loam soil. They used watermark sensors and suction cups (at 1.9 m depth) to estimate the drainage volumes and nitrate concentrations, respectively, and found nitrate concentrations ranging between 10 and 60 mg L^{-1}, which are comparable to those measured in this work at Barluenga. The soil nitrate concentration under the medium DS rate (315 kg N ha^{-1}) was significantly lower than that under the conventional fertiliser treatment (420 kg N ha^{-1}), and nitrate leaching under the medium DS rate was reduced by 20–32% in relation to that under mineral fertilisation.

In forage ryegrass–maize systems, Demurtas et al. [24] evaluated nitrate losses in sandy textured soil in northern Italy by measuring nitrate concentrations in soil solution via disk lysimeters. They reported that the nitrate concentrations at 0.90 m depth in a treatment that combined fertilisation with cattle slurry and mineral N were never higher than those using a mineral treatment with similar N application during the maize crop season, whereas during the winter crop period, the nitrate concentration was not associated with N fertilisation but with the natural water surplus during that period. Similar results were reported by Trindade et al. [2] in an experiment with different mineral and cattle slurry fertilisation treatments in northern Portugal in sandy loam soil. They suggested that it is possible in highly productive maize-ryegrass systems to fertilise using slurry exclusively at annual rates of up to 250 kg available N ha^{-1} (480 kg total N ha^{-1}) with minimal leaching losses. Compared with treatments that combined slurry and mineral fertilisation, slurry applications resulted in high yields and N absorption rates and a greater nitrogen use efficiency combined with a lower nitrate leaching potential. Additionally, Perego et al. [52] in the Po Valley in a loam textured soil, reported the possibility of using up to 294 kg ha^{-1} $year^{-1}$ of organic nitrogen without exceeding the 50 mg L^{-1} nitrate concentration threshold.

In Torremira, the average nitrate concentrations for the green pea, barley and maize seasons ranged between 60 and 858 mg L^{-1}, which were much higher than those at Barluenga, and in all cases exceeded the 50 mg L^{-1} threshold. The average nitrate concentrations for the whole experimental period, 274.8 and 295.8 mg L^{-1} for the P and M treatments, respectively, are considered high and are related to the scarce soil water retention capacity derived from the texture, shallow depth and stoniness [50]. Drainage is a driving factor for nitrate leaching in soils with these characteristics, and irrigation and fertilisation should be managed carefully to avoid excess water and drainage in these type of soils. However, even with the high risk of nitrate leaching that is associated with these soil characteristics, the nitrate concentrations in soil solution were not higher than those reported by Perego et al. [52] and Trindade et al. [46].

Compared with the mineral fertilisation treatment, the application of nitrogen in the form of pig slurry to green pea in the P treatment did not result in a significant increase in the nitrate concentrations in soil solution. This would indicate the capacity of this crop to adapt N fixation to the soil inorganic N content. This is corroborated by the study of Salmerón et al. [53] who analysed the behaviour of irrigated alfalfa under two rates of pig slurry application and a P-K fertilised control application in an experiment using lysimeters. The results of that study revealed that applications of pig slurry did not affect forage yields, total N extractions or nitrate loads in the drainage, but the plant $\delta^{15}N$ values were greater with pig slurry fertilisation than with the control, revealing the flexibility of alfalfa in adjusting symbiotic N fixation depending on mineral N availability.

5. Conclusions

The results of this work clearly show that increasing the substitution of mineral fertiliser with pig slurry over the amount of 170 kg N ha^{-1} established in the EU Nitrate Directive in highly N extractive maize double-cropping systems without increasing the risk for water nitrate contamination is possible. Although the substitution cannot be complete using traditional application systems (slurry tanks), as maize need some N at side-dressing to obtain optimal yields. With good pig slurry fertilisation management, it is possible to apply pig slurry to cover all the winter cereal N needs and ≈2/3 of the maize N requirements, up to 360 kg N ha^{-1} per year in this work. The weak point in slurry management is the field spreading of the required N rates. For this purpose, incorporating technical improvements in the distribution machinery, i.e., flow meters coupled with GPS and slurry nitrogen meters on the tanks, which could allow monitoring of the applied nitrogen dose and enable real-time adjustments in the short term, is key. The limitation of incomplete substitution of mineral N by slurry can be overcome via fertigation with the liquid fraction of slurries [54].

Thus, the nitrogen fertiliser values of slurries can be increased in double-cropping systems by considering their composition and adjusting the N rates and application systems and timing to meet the needs of each crop. This should lead to a reduction in the application of mineral fertilisers, nutrient surpluses and environmental pollution.

Supplementary Materials: The following supporting information can be downloaded at the website of this paper posted on Preprints.org, Figure S1: Average daily temperature and daily precipitation during the experimental period (SIAR network Z21_Tauste station); Figure S2: Pig slurry N total concentration estimated in the field by conductimetry and determined in laboratory. Figure S3: Ceramic suction cups. Installation in the field and extraction of the soil solution. Table S1: Nutrient concentration in pig slurry (Total N, P_2O_5 and K_2O, kg m^{-3}) applied to the pig slurry treatment in the different crops and years at the two sites. Table S2: Average maize yields in each of the three years, at the two sites and for the two treatments (P: pig slurry, M: synthetic fertilizer). N indicates the number of data points used to calculate the mean. In the same column, average yields followed by the same letter are not significantly different (Tukey’s test). Table S3: Average wheat yields in Barluenga in each of the years and for the two treatments (P: pig slurry, M: synthetic fertilizer). N indicates the number of data points used to calculate the mean. In the same column, average yields followed by the same letter are not significantly different (Tukey’s test). Table S4: Average green pea yields in Torremira in each of the years and for the two treatments (P: pig slurry, M: synthetic fertilizer). N indicates the number of data points used to calculate the mean. In the same column, average yields followed by the same letter are not significantly different (Tukey’s test). Table S5: Average values of the nitrogen use efficiency in the two treatments for each combination of crop × year.

Author Contributions: Conceptualization, D.Q., M.V. and A.D.; methodology, D.Q. and M.V.; formal analysis, D.Q. and B.M.; investigation, M.G., and B.M.; data curation, B.M. and M.G.; writing—original draft preparation, D.Q.; writing—review and editing, D.Q., M.G., M.V. A.D. and B.M; supervision, D.Q.; project administration, D.Q. and B.M.; funding acquisition, D.Q., M.V. and A.D. All authors have read and agreed to the published version of the manuscript

Funding: This research was funded by the Government of Aragón and the European Agricultural Funds for Rural Development - FEADER, grant GCP 2016-0033.

Data Availability Statement: The raw data supporting the conclusions of this article will be made available by the authors on request.

Acknowledgments: The authors thank to the Comunidad de Regantes n° XI de los riegos de Bardenas, Tauste Centro Gestor de Estiercoles S.L. and Cooperativa Agraria San Miguel de Tauste for their support and cooperation.

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

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