agronomy

Article

Nutrient Potential Leachability in a Sandy Soil Amended with Manure-Based Fertilisers

Joana Prado *, Paula Alvarenga, Henrique Ribeiro and David Fangueiro *

Linking Landscape, Environment, Agriculture and Food Research Center (LEAF), Associated Laboratory for Sustainable Land Use and Ecosystem Services (TERRA), Instituto Superior de Agronomia, University of Lisbon, Tapada da Ajuda, 1349-017 Lisbon, Portugal; palvarenga@isa.ulisboa.pt (P.A.); henriqueribe@isa.ulisboa.pt (H.R.)
* Correspondence: jprado@isa.ulisboa.pt (J.P.); dfangueiro@isa.ulisboa.pt (D.F.)

Abstract: The application of manure-based fertilisers (MBFs) is considered an important practice for achieving agricultural sustainability. However, the potential losses of nutrients to the environment need to be thoroughly evaluated. This study aimed to assess nutrients' potential leachability from a sandy soil, fertilised with MBFs produced by mixing manure from one single animal species with N- or P-mineral fertilisers, to achieve target N:P ratios (1:1, 2:1 and 0.5:1). MBFs were prepared by combining pig slurry, cattle slurry or poultry manure with N- and P-mineral fertilisers, or slurry-derived materials, obtained by solid–liquid separation. A leaching experiment was set-up in soil columns treated with MBFs, for 59 days, with seven leaching events. Poultry manure application to soil led to higher potential N leaching, while pig slurry induced higher P leaching. All 2:1 MBFs decreased P leaching, relative to the original manure, with the higher reduction (52%) being observed for pig slurry with urea. The addition of urea to poultry manure also diminished its potential for N leaching. The behaviour of P-enriched materials, pig slurry solid fraction and both 0.5:1 MBFs obtained with phosphoric acid addition showed a higher risk of P leaching, while the use of superphosphate as a P-mineral source decreased the risk of P leaching. Concluding, it is possible to use specific MBFs, enriched with N and P from mineral sources, and have lower N and P leaching potential, reducing the risks associated with manure soil application, while increasing their interest as alternative fertilisers.

Keywords: manure-based fertiliser; N:P ratio; nutrients leachability; macronutrients; micronutrients; nutrients availability

check for updates

Citation: Prado, J.; Alvarenga, P.; Ribeiro, H.; Fangueiro, D. Nutrient Potential Leachability in a Sandy Soil Amended with Manure-Based Fertilisers. *Agronomy* **2023**, *13*, 990. https://doi.org/10.3390/agronomy13040990

Academic Editors: Monika Mierzwa-Hersztek and Javier M. Gonzalez

Received: 1 February 2023
Revised: 9 March 2023
Accepted: 25 March 2023
Published: 28 March 2023

1. Introduction

Since World War II, agricultural developments have increased food production, with subsequent increases in the use of mineral fertilisers [1]. This higher food production has resulted, nowadays, in non-sustainable agricultural practices and a reduction in the organic matter and nutrient content of soil, culminating in lower productivity [1]. The concept of the circular economy has been promoted by the European Commission to achieve an eco-friendly agriculture, which would close the nutrient loop, by decreasing their losses, improving nutrient use efficiency, and diminishing the dependency on the import of energy and raw materials for mineral fertilisers production [2–4]. Subsequently, an emphasis on the application of recycled organic materials to soil emerged, to close the nutrient cycles, and improve soil health and quality, while protecting the environment, climate, and ecosystems [5]. The application of raw manure to soil is recognised as a practice for enhancing soil fertility and crop yield, especially since it contributes to restoring soil carbon reserves, improving carbon sequestration, and can also improve soil structure by increasing soil porosity [1,6].

To valorise manure as an essential resource by maximising the quantity of manure applied and nutrients recovery, it is necessary to alter some traditional practices and turn manure use more attractive to farmers. Nonetheless, manure utilisation as fertiliser faces some constraints, like the following facts: (i) nitrogen (N) and phosphorus (P) concentrations in manure are much lower than in mineral fertilisers [7]; (ii) only part of the nutrients are readily available for plants, the majority of the nutrients are present in the constitution of complex organic molecules, which need to be mineralised, making it difficult to assess their availability [8,9]; (iii) the quantity and frequency of manure application to crops are lower than the usual practice with mineral fertilisers [10]; and (iv) the costs of transporting and applying manures, especially slurries (liquid manure), may make the practice unsustainable [11]. As stated, nutrients' availability to plants is difficult to predict, and depends greatly on the animal species and on the water content of the material, i.e., if it is a solid manure or a slurry. For instance, according to Portuguese legislation, predictably, the available N content ranges between 1.3 and 2.5 kg m^{-3} in cattle slurry, between 14 and 21 kg t^{-1} in poultry manure, and between 3.0 and 4.2 kg m^{-3} in pig slurry [12]. Moreover, the availability of plant nutrients via manure application also relies on the soil characteristics, namely (i) the soil colloidal complex, which can retain nutrients [13], (ii) soil pH, which can influence the solubility of the nutrients (e.g., lower pH can increase P solubility) [14], (iii) soil composition, (e.g., soils with higher clay content will reduce nutrients losses, such as P [15]) and (iv) the microbiota, since soil microorganisms have extreme importance to the mineralisation of manure and to the release of plant essential nutrients [16].

However, manure application can also have negative impacts on soil and water [10], the most important of which is the non-point-source pollution with nutrients to the receiving hydrological system. The recommendations for fertiliser application are usually based on crops' N requirements, hence, manure application to soil results, in most cases, in the overapplication of P. This is the result of an unbalanced N and P ratio relative to crops demands [17]. When P application exceeds the crop offtake, it can cause the buildup of large amounts of P in the soil profile [18], a problem already faced by some countries in northwest Europe, which hinders the possibility of applying higher amounts of manures to soil [19], and ultimately can lead to potential P losses to the surface water bodies, causing eutrophication [20].

To overcome some of these problems, the concept of bio-based fertiliser is becoming more widely acknowledged, which suggests an even nutrient flow, while recovering materials, such as manures by improving its characteristics (e.g., nutrient concentration, nutrients availability, sanitisation) [21,22], and maintaining the benefits of organic fertiliser application. The production of a manure-based fertiliser (MBF) would combine the "more interesting" characteristics of the manures, i.e., organic matter content, and supply of both macro- and micronutrients essential for crops' healthy production, with some characteristics of mineral fertiliser, e.g., specific nutrients' ratio, higher nutrient concentrations and availability [10,11]. The MBFs may also appear as a solution for P overapplication to the soil by transforming the manures or altering their characteristics, to products that, for instance, can diminish the soil P saturation and restore soil P value to healthy levels, while taking advantage of their nutrients and organic matter content [19]. Modifying the N:P ratio in the manures by producing blends with an increase in the N:P ratio to values closer to the crop's N needs may avoid surplus P application. On the other hand, in some situations of soil P deficiency, it could be also interesting to evaluate the possibility of producing MBFs richer in P, for instance, producing blends with a 0.5:1 N:P ratio. The co-application of manure with mineral fertilisers, independent of the lower proportion of mineral fertilisers in the blend, may alter the leaching potential of the nutrients in the MBF compared to raw manures or their mineralisation rates, which may result in a decreased or increased risk of nitrate and P leaching from the soil and also induce an upsurge in the agronomic value of the MBFs [9,23].

This study aimed to evaluate the potential nutrient leaching of several MBFs, produced by blending manures with small quantities of mineral fertilisers to modify their N:P ratios to three specific ratios (1:1, 2:1, and 0.5:1). The first objective was to compare MBFs with the original raw manure to identify whether the addition of mineral fertiliser would induce an increase in the potential leaching compared to the raw manure. A second objective was to compare the MBFs within the same N:P ratio to identify which of the proposed MBFs would lead to the lower potential losses by leaching. The results were also used to assess the agronomic efficiency of these MBFs, considering that both macro- and micronutrients in the leachate are potentially available to the crop—plant-available nutrients. A higher nutrient leaching potential associated with a specific MBFs may indicate a higher risk of environmental problems and to a decrease in their agronomic value. More emphasis is given to N, P and K, but other macro- and micronutrients, and the leachates' pH and electrical conductivity, were also assessed.

2. Materials and Methods

2.1. Manure Sampling and Characterisation

The manures used in this experiment were all collected on farms representative of the Portuguese livestock system: (i) cattle slurry (CaS), collected from a commercial dairy farm, at Palmela; (ii) pig slurry (PiS), from a pig fattening farm located at Montijo; and (iii) poultry manure (PoM), sampled in a commercial farm specialised in the production of poultry meat, Herdade Daroeira, at Alvalade do Sado. Manure samples were stored at 4 °C, before characterisation and use, and analysed in triplicate with respect to their: dry matter content (DM), total organic carbon (TOC), total nitrogen (N_{Total}), ammonium nitrogen (NH_4^+-N), total phosphorus (P_{Total}, expressed as P_2O_5) and total K (K_{Total}, expressed as K_2O), using methodologies previously described by Prado et al. (2022). When the analytically determined NH_4^+ content of the manure (or MBF) was higher than the estimated N_{av}, the measured NH_4^+ content was used as the value of N_{av}. The composition of the three manures can be consulted in Table 1.

2.2. Preparation of Manure-Based Fertiliser Blends

The ratios considered were obtained by using the raw manures as a starting material for each potential MBF. The intended ratios, simply referred to as N:P ratios, were 0.5:1, 1:1 and 2:1, and were calculated by considering the plant's available N content and the total P content. The plant's available N content was assumed to be 60% of the total N, for manures with DM < 20%, and 50% of the total N, for manures with DM > 20% according to the recommendations of the Portuguese legislation [12]. As for the total P content, and only to calculate the N:P ratio, P was expressed as P_2O_5, since this is the form traditionally used to express P in the formulations of mineral fertilisers, allowing a clearer perspective of which type of nutrients ratios could be achieved with manure-based fertilisers. The raw materials (PiS: pig slurry, CaS: cattle slurry; PoM: Poultry manure) were used as the MBFs with the 1:1 ratio, since, based on their composition (Table 1), this corresponds to their approximate N:P ratios.

To obtain MBFs richer in N, i.e., with a 2:1 ratio, urea and ammonium sulphate were used as alternative materials, giving rise to the blends: PiS + U (pig slurry with urea), PiS + AS (pig slurry with ammonium sulphate), CaS + U (cattle slurry with urea), CaS + AS (cattle slurry with ammonium sulphate), PoM + U (poultry manure with urea), and PoM + AS (poultry manure with ammonium sulphate).

To obtain MBFs richer in P, i.e., with a 0.5:1 ratio, three possibilities were evaluated: the use of the solid fraction of the manure, which, in the case of pig manure, was adequate to achieve the desired N:P ratio, and the addition of superphosphate or phosphoric acid, as alternative materials, given rise to the blends: PiS-SOL (solid fraction from pig manure), CaS + SP (cattle slurry with superphosphate), CaS + PA (cattle slurry with phosphoric acid), PoM + SP (poultry manure with superphosphate), and PoM + PA (poultry manure with phosphoric acid).

The composition of the MBFs prepared from the blending of the manures with the mineral supplementation is presented in Table 1 and was calculated based on the raw manure and mineral fertilisers composition.

Table 1. Physicochemical characteristics of the raw manures (N:P ratio 1:1) and the manure-based fertilisers considered in the study (N:P ratios 2:1 and 0.5:1), all expressed on a fresh matter basis (mean value, n = 3). The quantity of manure and mineral fertiliser applied in each leaching column is also provided (with the percentage of the mineral in the blend), as well as the amount of nutrients vehiculated by those quantities per column.

		DM $g\ kg^{-1}$	TOC $g\ kg^{-1}$	N_{Total} $g\ kg^{-1}$	NH_4^+-N $g\ kg^{-1}$	N_{av} $g\ kg^{-1}$	P_{Total} $g\ kg^{-1}$	K_{Total} $g\ kg^{-1}$	Blend Composition		N_{Total} $mg\ kg^{-1}$	NH_4^+-N $mg\ kg^{-1}$	N_{av} $mg\ kg^{-1}$	P_{Total} $mg\ kg^{-1}$	K_{Total} $mg\ kg^{-1}$
									g Manure	g Mineral					
1:1 Ratio	PiS	129.74	55.00	8.41	5.64	5.64	2.49	2.84	13.87	-	116.67	78.24	70.00	34.40	39.26
	CaS	103.97	39.50	3.46	1.47	2.08	0.81	2.75	33.72	-	116.67	49.57	70.00	27.31	92.39
	PoM	749.36	352.10	20.3	3.54	10.15	5.16	15.41	6.90	-	140.00	21.66	70.00	35.45	105.86
2:1 Ratio	PiS + U	125.96	55.00	14.86	12.17	12.17	2.41	2.76	5.95	0.09 (1.3%)	86.47	70.00	70.00	14.75	16.83
	PiS + AS	125.76	55.00	14.6	11.91	11.91	2.41	2.75	5.98	0.19 (2.8%)	86.73	70.00	70.00	14.98	17.09
	CaS + U	103.59	39.52	5.13	3.15	3.75	0.81	2.74	18.6	0.07 (0.4%)	95.75	58.73	70.00	15.07	50.67
	CaS + AS	103.11	39.52	5.17	3.19	3.79	0.81	2.73	18.3	0.15 (0.8%)	95.32	58.91	70.00	14.82	50.13
	PoM + U	727.53	352.10	33.11	16.45	23.25	5.01	14.96	2.92	0.09 (2.9%)	99.67	49.51	70.00	15.02	44.86
	PoM + AS	702.53	352.10	32.16	16.07	22.64	4.83	14.44	2.90	0.19 (6.3%)	99.42	49.68	70.00	14.90	44.49
0.5:1 Ratio	PiS-SOL	232.5	96.77	10.93	6.45	6.45	4.76	3.67	12.81	-	140.00	82.62	70.00	60.84	46.75
	CaS + SP	103.45	39.50	3.44	1.46	2.07	1.72	2.73	33.72	0.17 (0.5%)	116.67	49.57	70.00	58.13	92.39
	CaS + PA	99.65	39.50	3.32	1.41	1.99	1.72	2.63	33.72	1.46 (4.2%)	116.67	49.57	70.000	60.38	92.39
	PoM + SP	743.67	352.10	19.9	3.08	9.95	8.65	15.11	6.90	0.14 (1.9%)	140.00	21.66	70.00	60.66	105.86
	PoM + PA	718.24	352.10	19.46	3.01	9.73	8.42	14.77	6.20	0.99 (13.8%)	140.00	21.66	70.00	54.34	105.86

PiS: pig slurry, CaS: cattle slurry; PoM: Poultry manure. PiS + U: pig slurry with urea; PiS + AS: pig slurry with ammonium sulphate; CaS + U cattle slurry with urea; CaS + AS: cattle slurry with ammonium sulphate; PoM + U: poultry manure with urea; PoM + AS: poultry manure with ammonium sulphate; PiS-SOL: solid fraction from pig manure; CaS + SP: cattle slurry with superphosphate; CaS + PA: cattle slurry with phosphoric acid; PoM + SP: poultry manure with superphosphate and PoM + PA: poultry manure with phosphoric acid. Dry matter: DM; Total organic carbon: TOC; N_{Total}: Total nitrogen; NH_4^+-N: Ammonium nitrogen; N_{av}: Available nitrogen (calculated as a % of the total N); P_{Total}: Total phosphorus; K_{Total}: Total potassium.

2.3. Leaching Experiment

The leaching experiment was performed with three repetitions per treatment, plus the control (soil without MBF). Each replicate was assembled with 1 kg of air-dried soil in PVC columns (30 cm long × 5.7 cm internal diameter). The soil used in this study was a sandy soil, classified as Haplic Arenosols [24], a sandy, very poor in both extractable P (4.33 mg kg^{-1} soil) and K (10.98 mg K kg^{-1} soil), total organic carbon close to 4.3 g kg^{-1} soil, and an initial pH of 5.6. This soil was chosen to maximise the leaching potential and compare the MBFs within the worst conditions in terms of leaching. The soil in the columns was saturated with water from the bottom by capillary rise, until it reached its full water holding capacity. The MBFs were applied to the soil top layer in the column, three days before the beginning of the leaching process, since manure cannot be applied before rainfall events, considering a prediction of a three-day meteorological forecast [25]. The amount of each material applied was calculated in order to supply the equivalent to 210 kg plant available N ha^{-1}. Considering the 0–20 cm topsoil layer and a soil density of 1.5 t m^{-3}, the amount of N applied was equivalent to 70 mg N kg^{-1} soil. The amounts of each manure or MBF (with an indication of the percentage of mineral fertiliser), applied to the column are provided in Table 1, considering the reference quantities, as well as the quantities of N_{Total}, NH_4^+-N, N_{av}, P_{Total} and K_{Total} vehiculated by each MBF.

Seven leaching events were planned, weekly during the first month and every two weeks during the second month. Therefore, the leaching events corresponded to days 3, 10, 17, 24, 38, 51, and 59 after the MBF application to soil. Columns were kept covered with perforated parafilm, to allow gaseous exchanges while minimising water loss by evaporation. Before each leaching event, the column was weighed, and water was added to keep soil moisture at a constant rate. The leaching event was intended to simulate rainfall and used 200 mL of distillate water, corresponding to the soil's maximum water holding capacity. The water was added gradually to each column and the leachate was collected in vials. The collecting vials were weighed, to measure the total volume of leachate collected, to be converted to volume by assuming a density of 1 g mL^{-1}. The electrical conductivity (EC) and pH of the leachate were measured directly in the collecting vials (AL15, Aqualytic, Portugal), and, after that, the samples were stored at 4 °C before analysis of the nutrients' concentrations. The soil column was sealed at the bottom by a glass wool layer and a PVC net. Hence, the leachates that were obtained did not have any suspended solids, and consequently, the nutrients present in the leachate were in a soluble form. Therefore, the nutrient concentrations measured in the leachate represent the fraction of the total, applied via the MBFs, that was soluble, i.e., those that may have impacted the quality of the received water, causing eutrophication. The N concentration was measured directly in the leachate by segmented flow autoanalyzer SAN plus (San Plus System, Skalar, The Netherlands) using the modified Berthelot method to measure NH_4^+-N [26] and rapid method for NO_3^--N [27]. The macro (N, P, K, calcium (Ca), magnesium (Mg) and sulphur (S)) and micronutrient (iron (Fe), copper (Cu), zinc (Zn) and manganese (Mn)) concentrations were also determined directly in the leachate by inductively coupled plasma optical emission spectrometry (iCAP 7000 Series ICP Spectrometer, Thermo Fisher Scientific, Waltham, MA, USA).

2.4. Statistical Treatment of Data

The statistical analyses were performed using one-way ANOVA for the 1:1 and 0.5:1 ratios, while for the 2:1 ratio, the factorial two-way ANOVA was used to estimate the interaction between the type of manure and mineral N source. To determine the statistical significance of the means, Tukey's test was performed, with a $p < 0.05$ and 95% degree of confidence. All statistical treatment of the data was performed with the software Statistix 7.

3. Results and Discussion

3.1. Potential Leachability of Nitrogen

In contrast with mineral fertilisers, organic materials have a significant amount of nutrients in organic forms, not readily available for plants [8]. The concentration of available nutrients relies on the mineralisation dynamic of the organic fraction, which will be responsible for releasing nutrients during a short or longer period, depending on its characteristics. For instance, as stated in the Introduction, N mineralisation soil characteristics, i.e., soils richer in organic matter, stimulate microorganism activity, hence contributing to a higher mineralisation rate [28]. Soil porosity is also an important soil property that informs the N mineralisation rate, because in soils with higher porosity, a higher oxygen content will promote a higher mineralisation rate [10]. On the other hand, higher N mineralisation rates will increase the concentrations of N mineral forms more rapidly, increasing the risk of N losses due to leaching, which will decrease the amount of available N to the plants and will decrease the value of manure fertilisation [29,30]. When fertilising with MBFs prepared with manure and small amounts of mineral fertilisers, it is important to assess the concentration of nutrients already present in available forms, prone to plant uptake, and that can cause water pollution when they are leached, because the plants are not using them.

Both slurries used in this study presented similar dynamics concerning the potential leaching of NH_4^+ (Figure 1a), stabilising the amount leached in the second week at ~4 mg NH_4^+-N kg^{-1} soil. Conversely, PoM presented a peak of NH_4^+ leached on day 10, ~9 mg NH_4^+-N kg^{-1} soil. In both slurries and PoM, on day 38 a second peak was observed, which can be attributed to some organic N mineralisation into NH_4^+, but also to previous low N leaching due to NH^{4+} immobilisation as a result of microorganism activity, and therefore N accumulation. Such initial immobilisation is usually observed after the application of slurry or solid manure to the soil as a result of the simultaneous application of C and N available to microorganisms [31]. Regarding the NO_3^- leached throughout the experiment (Figure 1b), only CaS presented a small amount of nitrate in the leachate (~2 mg NO_3^-N kg^{-1} soil) during the first 17 days, indicating that PoM and PiS presented a delay in nitrification, and consequently, a lower risk of nitrate leaching was expected. Indeed, since these materials were very poor in nitrate, the nitrate leached was exclusively due to the nitrification process and accumulation of NO_3^--N in the soil [25]. Gómez-Garrido et al. [32] also used pig slurry as a fertiliser and obtained similar results: a lower concentration of NO_3^- leached in the first weeks of the experiment. Nonetheless, especially with PoM application, the quantity of NO_3^- increased exponentially in the leachate until day 35. This was the material with the higher quantity of mineral N lost at the end of the experiment, ~54 mg N, representing ~67% of the Nav applied (Table 2), which was 2 times and 1.4 times higher than what was observed with CaS and PiS application, respectively. Consequently, in the absence of crop uptake or after sowing (reduced nutrient uptake), and with high precipitation, the potential risk of NO_3^- leaching may be high after the first month of PoM application. These results might also be used to appraise the N availability for plants, indicating that PoM application is more adequate for a crop with high N demands. For instance, it may be considered for a spring/summer crop, like maize, since this is a period during which lower rainfall is expected, and crops have higher N requirements. Still, caution should be adopted when PoM is applied to the soil, because even in the presence of a crop that absorbs part of the available N, it can contribute to an increase in the soil's N mineral forms, susceptible to subsequent leaching [33]. On the other hand, CaS presented the lowest quantity of total N lost at the end of the experiment, with only 30.82 mg N leached after 59 days, corresponding to the lowest percentages of N_{av} and N_{Total} leached among raw manures applied. This can suggest that the MBF made with CaS will have a lower risk of potential NO_3^- leaching, but might also induce lower N availability to the crops. Still, the cumulative value of NO_3^- leached after the application of the three manures did not exceed the European legal limit for nitrate leaching in vulnerable areas, even when applying the maximum quantity of 210 kg N indicated for these areas [34].

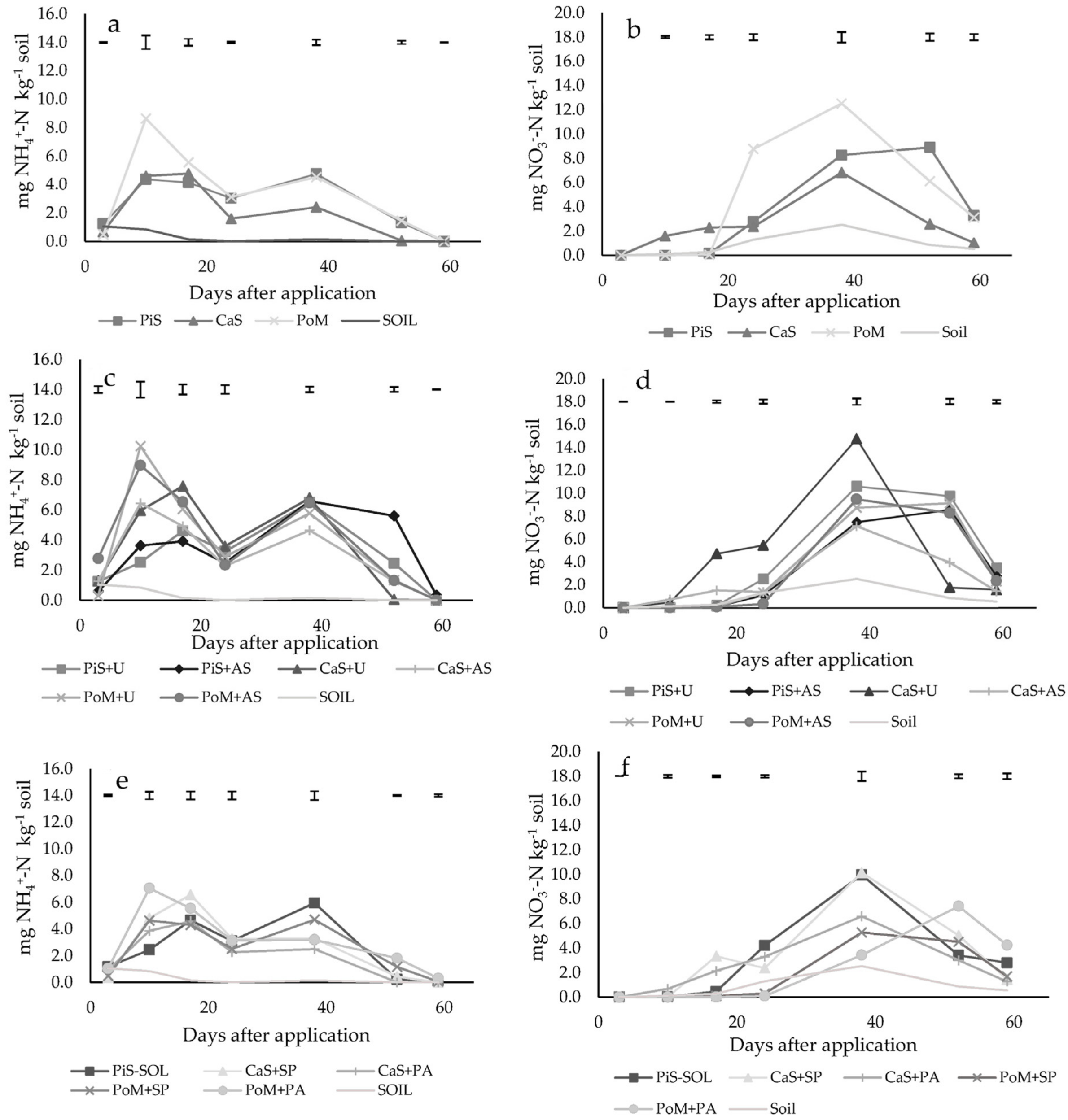

Figure 1. The quantity of NH_4^+ (**left**) and the NO_3^- (**right**) leached per column for each ratio 1:1 (**a**,**b**), 2:1 (**c**,**d**), and 0.5:1 (**e**,**f**) during the leaching events. The values presented are arithmetic means (n = 3). Bars represent the standard error values used for the comparison of the treatments via Tukey's test at each sampling date. PiS + U: pig slurry with urea; PiS + AS: pig slurry with ammonium sulphate; CaS + U cattle slurry with urea; CaS + AS: cattle slurry with ammonium sulphate; PoM + U: poultry manure with urea; PoM + AS: poultry manure with ammonium sulphate; PiS-SOL: solid fraction from pig manure; CaS + SP: cattle slurry with superphosphate; CaS + PA: cattle slurry with phosphoric acid; PoM + SP: poultry manure with superphosphate and PoM + PA: poultry manure with phosphoric acid.

Table 2. The cumulative values of the total mineral N (Min N), P, K, Ca, Mg and S leached throughout the experiment and the corresponding percentage of N, P and K conveyed by each blend. For each ratio in each column, the mean (n = 3) followed by different letters differ significantly for $p < 0.05$ (Tukey's test), the capital letters are the differences between the diverse manure-based fertilisers compared to the manure of origin, while the small letters correspond to the differences within each ratio.

		Min N			**P**		**K**		**Ca**		**Mg**		**S**	
		mg N	**% Nav**	**% Nt**	**mg P**	**% Applied**	**mg K**	**% Applied**	**mg Ca**	**% Applied**	**mg Mg**	**% Applied**	**mg S**	**% Applied**
1:1 Ratio	PiS	^{BC} 42.27 ^{b}	^{BC} 49.21 ^{b}	^{C} 29.53 ^{a}	^{B} 1.66 ^{a}	^{B} 2.45 ^{b}	^{A} 26.05 ^{c}	^{A} 60.79 ^{b}	^{A} 32.93 ^{b}	^{B} 25.11 ^{a}	^{A} 6.74 ^{b}	^{B} 12.85 ^{a}	^{B} 7.05 ^{b}	^{B} 43.78 ^{a}
	CaS	^{D} 30.82 ^{c}	^{D} 32.87 ^{c}	^{C} 19.72 ^{b}	^{C} 1.18 ^{b}	^{C} 3.71 ^{a}	^{A} 62.39 ^{b}	^{A} 65.17 ^{b}	^{C} 26.80 ^{c}	^{D} 18.20 ^{a}	^{B} 5.93 ^{b}	^{C} 11.08 ^{a}	^{C} 8.38 ^{b}	^{D} 32.04 ^{a}
	PoM	^{A} 54.49 ^{a}	^{A} 66.67 ^{a}	^{B} 33.34 ^{a}	^{BC} 1.17 ^{b}	^{B} 2.82 ^{b}	^{A} 84.86 ^{a}	^{A} 78.10 ^{a}	^{B} 41.91 ^{a}	^{C} 22.64 ^{a}	^{A} 8.33 ^{a}	^{C} 16.28 ^{a}	^{B} 16.90 ^{a}	^{B} 48.18 ^{a}
	SOIL	7.82 ^{d}	n.a	n.a	0.17 ^{c}	n.a	2.18 ^{d}	n.a	17.29 ^{d}	n.a	3.46 ^{c}	n.a	2.98 ^{c}	n.a
2:1 Ratio	PiS + U	^{A} 47.23 ^{b}	^{A} 56.30 ^{bc}	^{A} 44.34 ^{ab}	^{C} 0.77 ^{b}	^{A} 4.16 ^{b}	^{B} 12.67 ^{d}	^{A} 58.70 ^{ab}	^{A} 28.98 ^{c}	^{A} 42.51 ^{bc}	^{A} 5.88 ^{c}	^{A} 21.42 ^{c}	^{B} 5.07 ^{de}	^{A} 50.91 ^{b}
	PiS + AS	^{AB} 43.21 ^{c}	^{AB} 50.57 ^{c}	^{B} 39.83 ^{c}	^{BC} 1.05 ^{a}	^{A} 5.97 ^{a}	^{B} 12.38 ^{d}	^{A} 55.79 ^{abc}	^{A} 29.89 ^{c}	^{A} 43.63 ^{cd}	^{A} 5.95 ^{bc}	^{A} 21.79 ^{c}	^{A} 19.36 ^{c}	^{D} 1.09 ^{c}
	CaS + U	^{A} 53.80 ^{a}	^{A} 65.69 ^{a}	^{A} 48.02 ^{a}	^{C} 0.97 ^{ab}	^{B} 5.32 ^{ab}	^{B} 34.91 ^{ab}	^{A} 62.72 ^{bc}	^{C} 29.12 ^{c}	^{B} 40.89 ^{cd}	^{B} 6.23 ^{bc}	^{B} 22.46 ^{c}	^{C} 6.94 ^{de}	^{C} 42.37 ^{b}
	CaS + AS	^{C} 36.99 ^{d}	^{C} 41.68 ^{d}	^{B} 25.01 ^{d}	^{C} 1.00 ^{a}	^{B} 5.63 ^{ab}	^{B} 33.14 ^{bc}	^{A} 60.25 ^{c}	^{B} 36.07 ^{b}	^{A} 65.69 ^{a}	^{A} 7.44 ^{ab}	^{A} 32.64 ^{ab}	^{A} 27.46 ^{b}	^{E} 0.55 ^{c}
	PoM + U	^{B} 48.22 ^{b}	^{B} 57.73 ^{b}	^{A} 40.54 ^{c}	^{D} 0.84 ^{ab}	^{A} 4.51 ^{ab}	^{C} 29.96 ^{c}	^{B} 60.24 ^{c}	^{C} 32.76 ^{bc}	^{B} 32.59 ^{d}	^{B} 6.53 ^{bc}	^{B} 23.48 ^{bc}	^{B} 11.77 ^{cd}	^{A} 69.70 ^{a}
	PoM + AS	^{B} 48.90 ^{b}	^{B} 58.69 ^{b}	^{A} 41.32 ^{bc}	^{CD} 0.88 ^{ab}	^{A} 5.82 ^{ab}	^{C} 36.65 ^{a}	^{A} 75.78 ^{a}	^{A} 46.93 ^{a}	^{A} 60.79 ^{ab}	^{A} 8.36 ^{a}	^{A} 36.54 ^{a}	^{A} 43.96 ^{a}	^{D} 5.42 ^{c}
	SOIL	7.82 ^{e}	n.a	n.a	0.17 ^{c}	n.a	2.94	n.a	17.29 ^{d}	n.a	3.46 ^{d}	n.a	2.98 ^{e}	n.a
0.5:1 Ratio	PiS-SOL	^{C} 37.10 ^{b}	^{C} 41.86 ^{b}	^{D} 25.10 ^{a}	^{A} 4.19 ^{b}	^{A} 6.62 ^{b}	^{A} 26.51 ^{c}	^{B} 50.43 ^{c}	^{A} 30.61 ^{b}	^{C} 11.97 ^{b}	^{A} 6.51 ^{ab}	^{C} 6.95 ^{d}	^{B} 8.71 ^{c}	^{B} 31.75 ^{c}
	CaS + SP	^{B} 41.11 ^{a}	^{B} 47.56 ^{a}	^{B} 23.78 ^{b}	^{B} 1.77 ^{d}	^{D} 2.76 ^{cd}	^{A} 68.57 ^{b}	^{A} 71.04 ^{ab}	^{A} 40.71 ^{a}	^{C} 34.25 ^{a}	^{A} 8.40 ^{a}	^{B} 25.80 ^{a}	^{B} 15.39 ^{a}	^{B} 59.06 ^{b}
	CaS + PA	^{D} 31.10 ^{c}	^{D} 33.26 ^{c}	^{C} 16.63 ^{c}	^{A} 5.92 ^{a}	^{A} 9.53 ^{a}	^{A} 63.73 ^{b}	^{A} 65.80 ^{ab}	^{A} 40.53 ^{a}	^{B} 39.43 ^{a}	^{A} 7.91 ^{ab}	^{C} 19.15 ^{b}	^{B} 14.89 ^{a}	^{A} 67.69 ^{a}
	PoM + SP	^{D} 29.70 ^{c}	^{D} 31.26 ^{c}	^{D} 15.63 ^{c}	^{B} 1.25 ^{d}	^{C} 1.79 ^{d}	^{B} 70.98 ^{b}	^{B} 64.28 ^{b}	^{D} 29.03 ^{b}	^{D} 9.92 ^{b}	^{B} 6.20 ^{ab}	^{D} 8.97 ^{c}	^{B} 7.10 ^{c}	^{C} 22.84 ^{d}
	PoM + PA	^{C} 36.41 ^{b}	^{C} 40.26 ^{b}	^{C} 24.51 ^{ab}	^{A} 2.92 ^{c}	^{B} 3.90 ^{c}	^{A} 81.55 ^{a}	^{A} 74.27 ^{a}	^{C} 33.59 ^{ab}	^{D} 14.37 ^{b}	^{A} 7.45 ^{ab}	^{CD} 12.80 ^{c}	^{B} 11.14 ^{b}	^{C} 27.08 ^{c}
	SOIL	7.82 ^{d}	n.a	n.a	0.17 ^{e}	n.a	2.94 ^{d}	n.a	17.29 ^{c}	n.a	3.46 ^{c}	n.a	2.98 ^{d}	n.a

PiS + U: pig slurry with urea; PiS + AS: pig slurry with ammonium sulphate; CaS + U cattle slurry with urea; CaS + AS: cattle slurry with ammonium sulphate; PoM + U: poultry manure with urea; PoM + AS: poultry manure with ammonium sulphate; PiS-SOL: solid fraction from pig manure; CaS + SP: cattle slurry with superphosphate; CaS + PA: cattle slurry with phosphoric acid; PoM + SP: poultry manure with superphosphate and PoM + PA: poultry manure with phosphoric acid; n.a: not applicable.

The raw manures with the 1:1 ratio will be used as a reference to evaluate the results obtained for the NH_4^+ and NO_3^- potential leachability with the other two ratios used in the preparation of MBFs, i.e., the 2:1 (Figure 1c,d) and the 0.5:1 ratios (Figure 1e,f). The amount of NH_4^+ leached with the 2:1 and 0.5:1 MBFs in the first leaching event was residual, similar to the raw manures, since most of the leachate was composed of water existing in the soil before MBF application. In the second leaching event, the amount of NH_4^+ leached reflected the amount of mineral N applied via MBF. Additionally, as previously noted for the 1:1 manures, the peak of the amount of NH_4^+ leached occurred on day 38, ~6 mg NH_4^+-N kg^{-1} soil, which might be explained by organic N mineralisation, since most of the applied NH_4^+ was lost in the previous leaching events (Figure 1c).

Regarding nitrate leaching, a common trend was observed for all treatments: residual NO_3^- leaching until day 27, followed by an increase, with a plateau on days 38–50, and finally a decrease in the amount of nitrate leached, except for CaS + U and CaS + AS (Figure 1d). The combination of manure and mineral fertilisers seems to foment NO_3^- leaching, as emphasised by the results observed in CaS + U. Additionally, the different additives had repercussions for the slurries' potential NO_3^- leaching, but no disparity was observed relative to MBFs prepared with PoM. For instance, when ammonium sulphate was added to CaS, the N dynamic was similar to the raw CaS, leading to the lowest quantity of NO_3^- being leached within the 2:1 ratio, albeit still higher than the 1:1 CaS. Therefore, it is possible to conclude that the addition of urea to slurries stimulated the nitrification process, especially after the first 17 days, increasing the amount of NO_3^- leached. Indeed, the use of urea on its own, as previously described in a study by Scott et al. [35], increased the risk of NO_3^- leaching compared to the application of bovine urine in two different soils [35]. Additionally, a study demonstrated that by replacing 35% of the N applied via mineral fertiliser with chicken manure application, the N leachability was reduced when compared to the 100% of mineral fertiliser [36]. Adding either U or AS to PoM decreased the potential NO_3^- leaching associated with PoM in about ~13% of Nav and ~18% of N_{Total} leached when compared to raw PoM (Table 2), suggesting that the nitrification of NO_3^- was delayed in this case, mitigating the risk of leaching. Hence, producing a 2:1 MBF with PoM and either U or AS has been demonstrated to be a good option for farmers to adopt, and they can choose which additive better suits the needs of their crops. A previous study showed that the use of pellets that combined composted cattle manure with urea had a positive impact on the production of coriander, garden cress, and parsley plants [37].

P-enriched MBFs (0.5:1 ratio), with the addition of superphosphate or phosphoric acid, were also evaluated and, in these cases, the addition of a P source also diminished the NO_3^- leaching potential of PoM, indicating a possible nitrification inhibitor effect (Figure 1f). This could be attributed to the lower concentration of NH_4^+ observed during the experiments, which reduce the nitrification substrate (Figure 1e). Even though it can be beneficial for the environment and increase its value as fertiliser (i.e., lower losses, meaning that more nutrients will stay in the soil, and may eventually be used by the crop), it may also suggest that a lower quantity of N will be available to the crop in the short term and that a higher quantity of mineral fertilisers will be necessary to suppress the crop needs. P-enriched MBFs with PoM decreased the NO_3^- present in leachates, which could: (i) discard water pollution with NO_3^-, thereby resulting in a material with a higher fertilising value; and (ii) make these blends adequate for a less N-demanding crop. When considering an MBF adequate for a soil with low P concentration, i.e., with a 0.5:1 ratio, PiS-SOL, CaS + SP or CaS + PA can be considered good options, since they did not alter NO_3^- potential leaching, compared to the raw slurry (Table 2). Preserving the level of N leached, compared to the manure of origin, could indicate that, when these materials are applied, NO_3^- leaching problems are not expected, and that the N supply may be sufficient to satisfy the crops' needs (depending on the crop and soil utilised).

Relative to P, in a short time, PiS-SOL, CaS + PA and PoM + PA led to an increase in P leachability. Therefore, the application of these MBFs should be performed consciousness, knowing that they are only adequate for soils with lower P concentrations and with conditions not predisposed to leaching. Still, the long-term effects on the soil of the application of these MBFs are not yet known, even if it is well known that manure can increase the nutrient levels in the soil [4]. Consequently, more studies are still needed to promote the safe use of these MBFs.

3.2. Potential Leachability of Phosphorus

Phosphorus is an important macronutrient that can become one of the major factors limiting crop growth [38], and only a small part of the total P in the soil is available to the plant in the form of free orthophosphate ions [39]. The availability or leachability of this nutrient depends on several factors: (i) initial P concentration in soil, which is the reason for which a poor-P soil was used in this study; (ii) manure or derived product characteristics or application rate, which was analysed; (iii) tillage practices; (iv) irrigation regimes, which were kept constant between treatments; (v) soil pH, which influences the availability of orthophosphate ions; and (vi) clay content, which can increase P adsorption [14,40,41]. The amount of P applied via animal manure is, generally, higher than the amount exported by the plant, which may have two consequences: (i) P leaching, if the weather and soil conditions enhance this phenomenon; or (ii) P can be adsorbed onto the surface of reactive particles in the soil such as iron or aluminium oxides [42]. The evaluation of the three raw manures in terms of P leaching potential can be observed in Figure 2a. Except for a peak at day 24 for PiS, the P dynamics were similar among the three organic materials. Nonetheless, the cumulative amount of P lost by leaching throughout the 59 days of the experiment presented some differences. Bi et al. [43] reported that the combined application of organic and inorganic fertilisers formed a complex of stable phosphate, which mobilised the bacteria community and increased the phosphatase activity, improving P solubility. Indeed, PiS presented the highest quantity of leached P, 1.66 mg P kg^{-1} soil, while CaS presented the highest losses of total applied P (3.71%) (Table 2), which is in agreement with the fact that CaS supplied the lowest amount of P when applied to the column (Table 1). This might still be due to the fact that the P forms present in CaS are ultimately more soluble, and therefore more susceptible to leaching. Nevertheless, this is still a very low percentage of P leached, and the conditions of the experiment do not account for the P absorption by the crop, which would also counteract P leaching. Therefore, CaS was proven to be the manure with the highest P availability, but caution must be adopted when considering the soil to which CaS is to be applied, because higher P availability can lead to higher P leaching. The soil used in this study was a sandy soil with low clay content in order to maximise the leaching conditions. Nevertheless, independent of the manure applied to the soil, the amount of P leached was low, which is in accordance with the results from a study by Tiecher et al. [39], which also reported negligible P losses in a field experiment after successive application of PiS. Still, McDowell et al. [44] determined that the application of superphosphate, with or without cattle manure, resulted in lower P sorption, and that the leaching of P was substantial. Hence, when applying MBFs, the fertilisation plan should consider this risk.

Comparing the P leached by the N-enriched MBFs (i.e., 2:1 ratio) over the 59 days of leaching events, no differences could be observed between the two sources of N, urea and ammonium sulphate, with no differences observed in terms of cumulative P leached (Figure 2c and Table 2). Nonetheless, ammonium sulphate added to PiS slightly increased the quantity of P leached compared to the addition of urea, with 1.05 and 0.77 mg P kg^{-1} soil of cumulative P leached by PiS + AS and PiS + U, respectively, but PiS + U decreased that value relative to the raw PiS, which was 1.66 mg P kg^{-1} soil.

The addition of ammonium sulphate, an acidic mineral fertiliser, to PiS might have increased the P solubility, as commonly observed in acidified slurry [45], which could explain why a higher amount of P was lost in PiS + AS relative to PiS + U (Table 1). However, it should be highlighted that, independent of the manure used or the N source, the quantity of P leached from the MBF application was considerably lower than after the application of the corresponding raw material (even if the difference was statistically significant only for PiS + U). This can be attributed to the quantity of fertiliser required to supply the same amount of N to the soil being lower using a 2:1 ratio fertiliser. Hence, using a manure supplied with an N source diminished the risk of P leachability, making it adequate for use in P-saturated soils, avoiding environmental problems and guaranteeing healthy soils [19]. The PiS + U, PiS + AS, and CaS + AS MBFs may avoid the overapplication of P to the soil, and reduce the risk of leaching, which is a major concern in northern Europe [19].

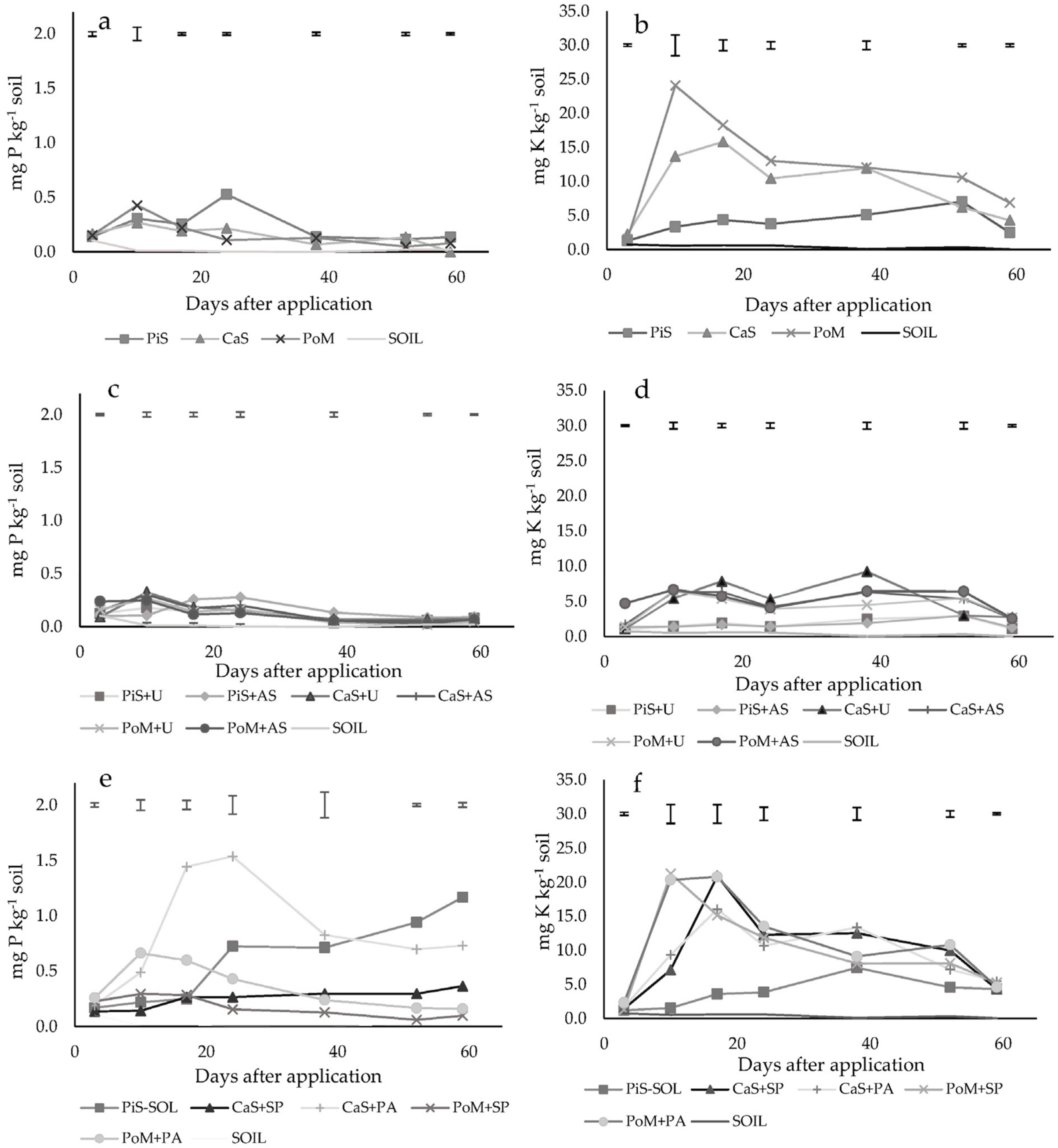

Figure 2. The P (**left**) and the K (**right**) concentrations on the leached for each 1:1 ratio (**a**,**b**), 2:1 (**c**,**d**) and 0.5:1 (**e**,**f**) during the leaching events. The vertical bars represent the standard errors for the means when performing the Tukey's test (n = 3). PiS + U: pig slurry with urea; PiS + AS: pig slurry with ammonium sulphate; CaS + U cattle slurry with urea; CaS + AS: cattle slurry with ammonium sulphate; PoM + U: poultry manure with urea; PoM + AS: poultry manure with ammonium sulphate; PiS-SOL: solid fraction from pig manure; CaS + SP: cattle slurry with superphosphate; CaS + PA: cattle slurry with phosphoric acid; PoM + SP: poultry manure with superphosphate and PoM + PA: poultry manure with phosphoric acid.

Kang et al. [46], after their study with poultry manure and pig slurry, demonstrated that, in the long term, P losses via leaching were a consequence of organic P mineralisation. Hence, having MBFs P enriched with a fraction of P via mineral fertiliser might have reduced P losses, to some degree, since P mineralisation takes longer to occur. The P potential leachability dynamics were quite different for the different solutions evaluated (Figure 2e), and with considerably higher cumulative P losses (Table 2). Organic P compounds, once dissolved, have a lower affinity to sorption onto soil particles, which occurs when these materials are applied to the soil [44], while, on the other hand, the addition of a mineral P source may have stimulated P leaching. For the first 10 days, the addition of phosphoric acid to PoM and CaS enhanced the potential of P leaching, more pronouncedly in the case of CaS + PA, reaching a plateau from days 17 to 24, at ~1.50 mg P kg^{-1} soil (Figure 2e). The addition of a liquid P source, phosphoric acid, to liquid manure, CaS, may have strengthened the P leachability when compared to its addition to PoM, also because of the acidic properties of phosphoric acid, thus increasing the solubility of P in slurry [45]. Independent of the manure used, the addition of phosphoric acid increased the cumulative P leached, four times for PoM + PA, and almost six times for CaS + PA, relative to the original manures (Table 2). Nonetheless, the enhancement of PoM with superphosphate maintained the risks of P leaching compared to PoM (1:1 N:P ratio). This is an advantage compared to the use of raw manure, which has resulted in the overapplication of P and, in extreme cases, culminated in environmental problems related to P. From day 17 onward, the use of PiS-SOL started to induce P losses, with an exponential growth from day 38 onward. Therefore, the application of PiS-SOL to the soil also considerably increases the quantity of P potentially leached relative to the raw slurry (PiS in 1:1 ratio), with approximately a 4-fold increase, thus increasing the environmental risks. It is known that the application of manure can improve P availability by enhancing the biological cycle [47]. Therefore these MBFs (0.5:1 ratio) were planned for soils that are very poor in P, where this increase in plant available P could be beneficial, agronomically speaking, since there would be a crop to assimilate P. Based on the total amount of P lost, P will be most prone to leaching, particularly in sandy soils like the one used in this study, when using PoM + PA, PiS-SOL and CaS + PA, in ascending order. Still, notably, the cumulative value leached, even if higher than the value observed in 1:1 raw manure, was still low.

3.3. Potential Leachability of Potassium

The origin of K in the production of mineral fertilisers is not renewable, since it comes from potash ore, the largest reserve of which is in Canada, making the EU dependent on its import [48]. Therefore, it is very important to consider alternative materials that are rich in K in order to change fertilisation practices and use manure, or these MBFs, as an alternative K fertiliser.

PoM was the manure resulting in the highest K losses due to leaching in the first ten days, reaching a peak at ~25 mg K kg^{-1} soil (Figure 2b), which also indicates a higher availability of K to crops with the application of that manure. This has been explained by some authors with reference to the fact that K in poultry manure is more labile than in mineral fertilisers [49]. After analysing the dynamics of K over the 59 days of the experiment (Table 1), it appears that PoM leached 80% of the total K applied, while the slurries exhibited lower leaching potential, ~66% of the total K applied. Potassium is a macronutrient required in large quantities to optimise growth and productivity, since it is essential for physiological mechanisms and metabolism processes in plants [50]. A large amount of manure's K is in a mineral form, and K is exported in high quantities by plants. Therefore, when applied to a crop, the concentration of K in leachate would be expected to be residual [15]. Comparing the two slurries from an agronomical perspective, CaS will supply a higher amount of K than the other slurry, which can be essential for the fertilisation of some crops in soils with low concentrations of plant-available K.

The dynamic of K was relatively similar among the different 2:1 MBFs (Figure 2d), and the percentage of K leached relative to that applied was also statistically similar, but with a clear reduction in the quantity of K leached relative to the raw manures (Table 2). The explanation for this is the same as that already provided for P: the reduction in the quantity of the 2:1 blend necessary to apply when using the 2:1 ratio to supply the same amount of mineral N (Table 1). These differences are important to consider when assessing the use of these MBFs in different soils, with different concentrations of extractable K. Since the K present in the soil is mostly in forms unavailable to plants, such as crystalline structures, the addition of an organic material that can "release" soluble K more easily and in higher amounts (e.g., the raw slurries, CaS and PoM) would make a difference in K-poor soils [50]. Macholdt et al. [51] observed, in a long-term field experiment, the positive effect of combining mineral fertilisers and manures, with an increase in the total and plant-available nutrient concentration in the soil.

From day one, the amount of K leached increased exponentially when a P source was added to either PoM or CaS (Figure 2f), subsequently decreasing. Alfaro et al. [52] observed that after the application of slurry, K was lost immediately, as observed in the raw manure and after the application of the 0.5:1 N:P ratio MBF. However, adding superphosphate to PoM slightly reduced the amount of K leached, compared to PoM, while the combination of CaS and superphosphate resulted in a small increase in the K leached compared to CaS (Table 2). Independent of the MBFs produced, the behaviour of the mixture (manure + mineral fertiliser), did not exhibit a trend, making it difficult to state what can be expected. Even if K is not as problematic as N and P in terms of environmental impacts, this nutrient is a mobile ion, and significant losses by leaching might occur, particularly in sandy soils [52].

3.4. Potential Leachability of Macronutrients

The shortage of macronutrients has repercussions on crop yield and quality (de Bang et al., 2021). Due to the rich composition of manure, with a single application, crops received different sorts of macronutrients. This effect can be observed through the concentration of N, P, K, Ca, Mg, and S in the leachates (Table 2; more complete information is in the Supplementary Materials, Figure S1).

Among the three raw manures (1:1 ratio), PoM presented the highest amount of Ca leached, ~42 mg Ca kg^{-1} soil, while CaS presented the lowest cumulative quantity of Ca leached, ~27 mg Ca kg^{-1} soil (Table 2). This is important when considering that Ca, in the form of calcium carbonate, is important for occluding soil organic carbon and subsequently ameliorates soil aggregation [53]. Yet, it has been reported that, after intensive fertilisation with cattle slurry, the percentage of Ca leached is between 47 and 51% of the total Ca applied [54]. That study was conducted after several years of manure application, which increased the nutrient leaching. Therefore, the long-term effect of MBF application in different types of soil should be assessed, in order to better understand what the consequences of their use in agriculture fields might be. The use of an N source, producing the 2:1 ratio MBFs, increased the percentage of Ca released from the mixture and the addition of a P source to manure doubled the concentration of Ca in the leachate in CaS + SP and CaS + PA, but the opposite was observed in PoM + SP and PoM + PA.

Magnesium is an important nutrient for the formation of chlorophyll and the structure of the chloroplast [55]. To allow crops to absorb Mg, it is essential to convert the mineral and organic magnesium into a water-soluble form, as represented in Table 2. Since the unique exogenous source of Mg was the manure, no major differences were observed when applying different MBFs to the soil. It can be stated that the enrichment of N or P in the blends did not affect the potential leaching of Mg or, from a different perspective, the potential availability of Mg to the plant. Caution should be taken when considering this, because in the long term, close to 50% of the total Mg can be lost via leaching [54].

The application of PoM to the soil resulted in double the amount of S being leached compared to the application of slurries (Table 2). In the case of PoM, the higher S availability can induce an improvement in nutrient assimilation by the plant, especially N fixation, and S is part of the organic metabolites and is a cellular component [56]. In the 2:1 ratio, the greatest differences were obtained when using ammonium sulphate due to the higher enrichment in S in the form of sulphate relative to the use of urea. This improvement resulted in an increase in the amount of S leached, which was 2.8, 2.3, and 2.6 times higher in PiS + AS, CaS + AS and PoM + AS, respectively, relative to the original raw manure. This extra addition of S to soil might be relevant, since in recent decades, in Northern Europe, the S content of the soil has diminished [57]. Even though the amount of S leached was higher when ammonium sulphate was added to the manures, the percentage of S leached, compared to the S amount applied to soil, was close to 1% in the slurries and close to 5% in PoM. This indicates that only a small fraction of S was leached, and that S was released slowly. The addition of a P mineral source to the manures in order to obtain the 0.5:1 ratio doubled the quantity of S in the leachate in the CaS blends, while in the PoM blends, the S leached was reduced to half, which was more noticeable with superphosphate (Table 2). This demonstrates that amending liquid and solid manure with a P source had different consequences: in slurries it stimulated S leaching, while for solid manure it delayed its release. In soils with S deficiency, PiS + AS, CaS + AS and PoM + AS would be a good solution to consider if the crop has a higher S demand; otherwise, S will be leached.

The deficiency of micronutrients may not have such a significant effect on crop yield, as the shortage in macronutrients [56], but they are important when other nutrients are missing, and ameliorate plants' homeostasis [58]. The extent of leaching of Fe, Cu, Zn and Mn can be consulted in the Supplementary Materials (Figures S2 and S3). This information is also pertinent since manure can vehiculate heavy metals such as Zn and Cu, which are regulated by law [40]. Liu et al. [40] stated that the application of manure by providing heavy metals can alter the biogeochemical cycle of these elements, and, if manure is applied at a higher rate, can create a potential risk of heavy metal leaching, ultimately contaminating soils. Still, the values observed for cumulative leaching were residual, even after one application of MBFs and under conditions that promote maximal leaching. Therefore, it is possible to state that the application of MBFs did not promote a risk of heavy metal contamination. Nonetheless, this is the first study conducted with these MBFs, and no long-term effects were evaluated. For instance, in a study in which cattle manure was applied for five consecutive years, the authors concluded that it was vital to adopt mitigation measures due to the increased concentration in the soil [59]. Additionally, Fe can alter the P solubility and reduce P leachability through the precipitation of a complex of Fe and P [60].

3.5. Effects on Leachate Electric Conductivity and pH

Electric conductivity (EC) and pH can affect plant growth, since both properties affect the availability and uptake of nutrients [61]. In this study, major differences were observed in the EC of the leachates (Figure 3), but not in their pH values (Figure S4). The EC is an indicator of soil-soluble salt concentrations, which, when excessive, may hinder the soil's health, affecting the plant's ability to absorb water and nutrients from the soil [62,63]. The application of fertilisers necessarily results in an increase in soil salinity (secondary salinisation), with a concomitant increase in the EC of the leachate produced from that soil, which could also serve as a nutrient availability indicator [64].

The EC of the leachates gradually decreased throughout the 59 days of leaching, being higher for the first two leaching events, on days 3 and 10 (Figure 3). The MBFs that presented the highest EC were PoM, CaS, PoM + SP and CaS + PA, which is in agreement with the results shown in the previous section (Figures 1 and 2). Nevertheless, it is important not to neglect the contribution of the micronutrients to this increase in the EC of the leachate (e.g., Fe, Cu, Zn and Mn; Figures S2 and S3), some added by the application of the fertilisers to the soil.

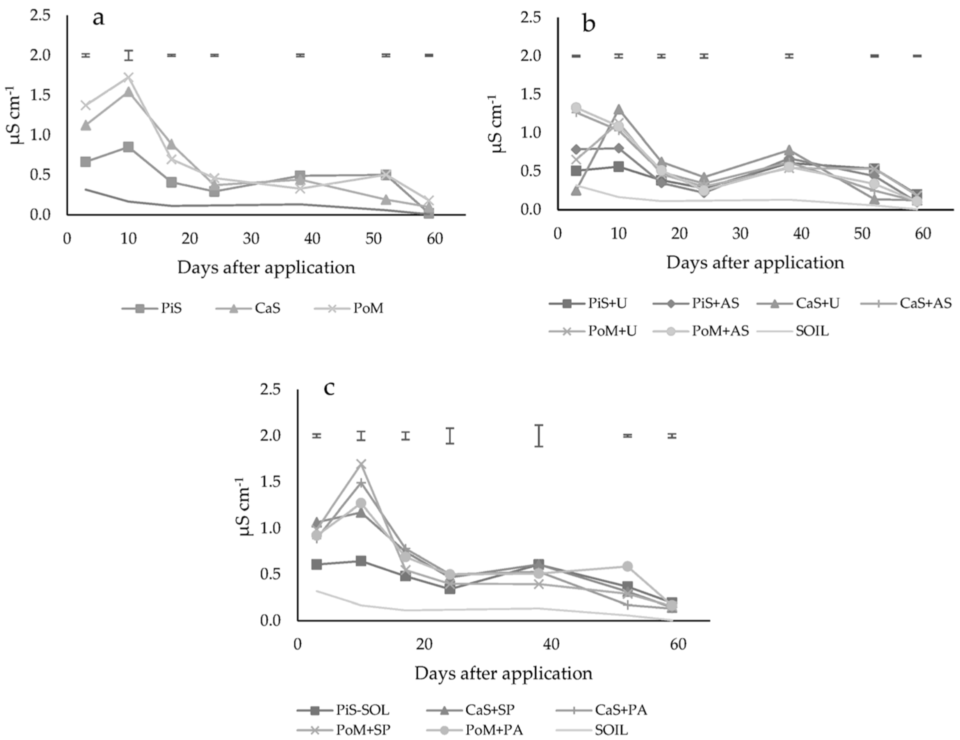

Figure 3. The electrical conductivity in the leachate over the duration of the experiment for the 1:1 ratio (**a**), 2:1 ratio (**b**), and 0.5:1 ratio (**c**). Bars represent the standard error values used for comparison of the treatments in the Tukey's test at each sampling date. PiS + U: pig slurry with urea; PiS + AS: pig slurry with ammonium sulphate; CaS + U cattle slurry with urea; CaS + AS: cattle slurry with ammonium sulphate; PoM + U: poultry manure with urea; PoM + AS: poultry manure with ammonium sulphate; PiS-SOL: solid fraction from pig manure; CaS + SP: cattle slurry with superphosphate; CaS + PA: cattle slurry with phosphoric acid; PoM + SP: poultry manure with superphosphate and PoM + PA: poultry manure with phosphoric acid.

4. Conclusions

The soil application of the proposed MBFs, with distinct N:P ratios, had repercussions on the potential nutrient leaching, demonstrating that the use of these MBFs might have specific impacts on water quality. The potential of nutrient leaching decreased with time, indicating that the first 24 days after application are the most problematic in terms of potential leaching.

Within the 1:1 ratio, PoM led to the highest potential leaching of N, K, Ca and S, indicating that this manure has, on one hand, the highest concentration of nutrients available to plants, but, on the other hand, it presents a higher risk of water pollution in soil prone to leaching.

The application of urea or ammonium sulphate to PoM mitigated the potential of NO_3^- leaching compared to raw PoM, which may predispose these MBFs to be used for winter crops. On the other hand, the addition of urea to slurries, especially to CaS, exponentially increased the risks of NO_3^- leaching. An important feature, common to all the N-enriched MBFs, was the decrease in the leaching potential of P, turning them into an important option for lowering the risk of their use in P-saturated soils. One other important feature, not addressed in this study, were the benefits of organic matter application, which are also dependent on soil characteristics.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/agronomy13040990/s1, Figure S1: The cumulative leaching of macronutrients leachate for each 1:1, 2:1 and 0.5:1 ratio; Figure S2: The iron (left) and the copper (right) concentrations on the leachate for each 1:1, 2:1 and 0.5:1 ratio during the leaching events.;

Figure S3: The zinc (left) and the manganese (right) concentrations on the leachate for each 1:1, 2:1 and 0.5:1 ratio during the leaching events.; Figure S4: The pH dynamics in the leachate for each 1:1, 2:1 and 0.5:1 ratio during the leaching events.

Author Contributions: Conceptualisation, J.P., H.R., P.A. and D.F.; methodology, J.P., H.R., P.A. and D.F.; validation, J.P., H.R., P.A. and D.F.; formal analysis, J.P., H.R., P.A. and D.F.; investigation, J.P., H.R., P.A. and D.F.; resources, D.F.; data curation, J.P., H.R., P.A. and D.F.; writing—original draft preparation, J.P., H.R., P.A. and D.F.; writing—review and editing, J.P., H.R., P.A. and D.F.; visualisation, J.P., H.R., P.A. and D.F.; supervision, D.F.; project administration, D.F.; funding acquisition, D.F. All authors have read and agreed to the published version of the manuscript.

Funding: This study was supported by the Project Nutri2Cycle: H2020-SFS-30-2017—"Transition towards a more carbon and nutrient efficient agriculture in Europe", funded by the European Union, Program Horizon 2020 (Grant Agreement No 773682), and by the logistic and institutional support of LEAF (Linking Landscape, Environment, Agriculture and Food Research Unit), funded by FCT (UID/AGR/04129/LEAF).

Data Availability Statement: Shared when requested.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

References

1. Rayne, N.; Aula, L. Livestock Manure and the Impacts on Soil Health: A Review. *Soil Syst.* **2020**, *4*, 64. [CrossRef]
2. Ritzén, S.; Sandström, G.Ö. Barriers to the Circular Economy—Integration of Perspectives and Domains. *Procedia CIRP* **2017**, *64*, 7–12. [CrossRef]
3. Spiegal, S.; Kleinman, P.J.A.; Endale, D.M.; Bryant, R.B.; Dell, C.; Goslee, S.; Meinen, R.J.; Flynn, K.C.; Baker, J.M.; Browning, D.M.; et al. Manuresheds: Advancing Nutrient Recycling in US Agriculture. *Agric. Syst.* **2020**, *182*, 102813. [CrossRef]
4. Svanbäck, A.; McCrackin, M.L.; Swaney, D.P.; Linefur, H.; Gustafsson, B.G.; Howarth, R.W.; Humborg, C. Reducing Agricultural Nutrient Surpluses in a Large Catchment—Links to Livestock Density. *Sci. Total Environ.* **2019**, *648*, 1549–1559. [CrossRef]
5. Möller, K.; Oberson, A.; Bünemann, E.K.; Cooper, J.; Friedel, J.K.; Glæsner, N.; Hörtenhuber, S.; Løes, A.K.; Mäder, P.; Meyer, G.; et al. Improved Phosphorus Recycling in Organic Farming: Navigating Between Constraints. *Adv. Agron.* **2018**, *147*, 159–237. [CrossRef]
6. Hoover, N.L.; Law, J.Y.; Long, L.A.M.; Kanwar, R.S.; Soupir, M.L. Long-Term Impact of Poultry Manure on Crop Yield, Soil and Water Quality, and Crop Revenue. *J. Environ. Manage.* **2019**, *252*, 109582. [CrossRef]
7. Ozlu, E.; Kumar, S. Response of Soil Organic Carbon, PH, Electrical Conductivity, and Water Stable Aggregates to Long-Term Annual Manure and Inorganic Fertilizer. *Soil Sci. Soc. Am. J.* **2018**, *82*, 1243–1251. [CrossRef]
8. De Boer, H.C. *Nitrate Leaching from Liquid Cattle Manure Compared to Synthetic Fertilizer Applied to Grassland or Silage Maize in the Wageningen, Netherlands*; Report 1055; Wageningen Livestock Research: Wageningen, The Netherlands, 2017.
9. Li, P.; Lang, M.; Li, C.; Thomas, B.W.; Hao, X. Nutrient Leaching from Soil Amended with Manure and Compost from Cattle Fed Diets Containing Wheat Dried Distillers' Grains with Solubles. *Water. Air. Soil Pollut.* **2016**, *227*, 393. [CrossRef]
10. Iqbal, A.; He, L.; Khan, A.; Wei, S.; Akhtar, K.; Ali, I.; Ullah, S.; Munsif, F.; Zhao, Q.; Jiang, L. Organic Manure Coupled with Inorganic Fertilizer: An Approach for the Sustainable Production of Rice by Improving Soil Properties and Nitrogen Use Efficiency. *Agronomy* **2019**, *9*, 651. [CrossRef]
11. Silva, A.A.; Carvalho, M.; Vasconcelos, E.; Fangueiro, D. Dairy Slurry Application to Stubble-Covered Soil: A Study on Sustainable Alternatives to Minimize Gaseous Emissions. *Agronomy* **2022**, *12*, 1021. [CrossRef]
12. MADRP, Ministério da Agricultura do Desenvolvimento Rural e das Pescas, 2018. Diário da República no25/2018. 2 Series, Lisboa. Available online: https://files.dre.pt/2s/2018/02/025000000/0413204170.pdf (accessed on 27 April 2022).
13. Xu, R.K.; Qafoku, N.P.; Van Ranst, E.; Li, J.Y.; Jiang, J. *Adsorption Properties of Subtropical and Tropical Variable Charge Soils: Implications from Climate Change and Biochar Amendment*; Elsevier Inc.: Amsterdam, The Netherlands, 2016; Volume 135, ISBN 9780128046937.
14. da Silva Cerozi, B.; Fitzsimmons, K. The Effect of PH on Phosphorus Availability and Speciation in an Aquaponics Nutrient Solution. *Bioresour. Technol.* **2016**, *219*, 778–781. [CrossRef]
15. Girotto, E.; Ceretta, C.A.; Lourenzi, C.R.; Lorensini, F.; Tiecher, T.L.; Vieira, R.C.B.; Trentin, G.; Basso, C.J.; Miotto, A.; Brunetto, G. Nutrient Transfers by Leaching in a No-Tillage System through Soil Treated with Repeated Pig Slurry Applications. *Nutr. Cycl. Agroecosystems* **2013**, *95*, 115–131. [CrossRef]
16. Pahalvi, H.N.; Rafiya, L.; Rashid, S.; Nisar, B.; Kamili, A.N. *Microbiota and Biofertilizers, Ecofriendly Tools for Reclamation of Degraded Soil Environs*; Chapter I; Dar, G., Bhat, R.A., LMehmood, M.A., Hakeemm, K.R., Eds.; Springer Nature Switzerland: Berlin/Heidelberg, Germany, 2022; Volume 2, ISBN 9783030610098.

17. Oenema, O.; Lesschen, J.P.; Rietra, R.; Rieger, J.; Hendriks, C. D.1.3 Driving Forces of Farming Systems and Their Impacts on CNP Ratios and Flows. 2021, pp. 1–91. Available online: http://nutri2cycle.eu/driving-forces-of-farming-systems-and-their-impactson-cnp-ratios-and-flows/ (accessed on 26 June 2022).
18. Chardon, W.J.; Aalderink, G.H.; van der Salm, C. Phosphorus Leaching from Cow Manure Patches on Soil Columns. *J. Environ. Qual.* **2007**, *36*, 17–22. [CrossRef]
19. Vanden Nest, T.; Ruysschaert, G.; Vandecasteele, B.; Houot, S.; Baken, S.; Smolders, E.; Cougnon, M.; Reheul, D.; Merckx, R. The Long Term Use of Farmyard Manure and Compost: Effects on P Availability, Orthophosphate Sorption Strength and P Leaching. *Agric. Ecosyst. Environ.* **2016**, *216*, 23–33. [CrossRef]
20. Liu, J.N.; de Neergaard, A.; Jensen, L.S. Increased Retention of Available Nitrogen during Thermal Drying of Solids of Digested Sewage Sludge and Manure by Acid and Zeolite Addition. *Waste Manag.* **2019**, *100*, 306–317. [CrossRef]
21. Chojnacka, K.; Moustakas, K.; Witek-Krowiak, A. Bio-Based Fertilizers: A Practical Approach towards Circular Economy. *Bioresour. Technol.* **2020**, *295*, 122223. [CrossRef]
22. Tur-Cardona, J.; Bonnichsen, O.; Speelman, S.; Verspecht, A.; Carpentier, L.; Debruyne, L.; Marchand, F.; Jacobsen, B.H.; Buysse, J. Farmers' Reasons to Accept Bio-Based Fertilizers: A Choice Experiment in Seven Different European Countries. *J. Clean. Prod.* **2018**, *197*, 406–416. [CrossRef]
23. Huang, J.; Duan, Y.; Xu, M.; Zhai, L.; Zhang, X.; Wang, B.; Zhang, Y.; Gao, S.; Sun, N. Nitrogen Mobility, Ammonia Volatilization, and Estimated Leaching Loss from Long-Term Manure Incorporation in Red Soil. *J. Integr. Agric.* **2017**, *16*, 2082–2092. [CrossRef]
24. FAO, Food and Agriculture Organization of the United Nations. *Guidelines for Soil Description*, 4th ed.; FAO: Rome, Italy, 2006; ISBN 9251055211.
25. Fangueiro, D.; Surgy, S.; Napier, V.; Menaia, J.; Vasconcelos, E.; Coutinho, J. Impact of Slurry Management Strategies on Potential Leaching of Nutrients and Pathogens in a Sandy Soil Amended with Cattle Slurry. *J. Environ. Manag.* **2014**, *146*, 198–205. [CrossRef]
26. Krorn, M. Spectrophotometric A Study of a Determination of Ammonia: Modified Berthelot Reaction Using Salicylate and Dichloroisocyanurate. *Analyst* **1956**, *81*, 677. [CrossRef]
27. Singh, J.P. A Rapid Method for Determination of Nitrate in Soil and Plant Extracts. *Plant Soil* **1988**, *110*, 137–139. [CrossRef]
28. Soler-Jofra, A.; Pérez, J.; van Loosdrecht, M.C.M. Hydroxylamine and the Nitrogen Cycle: A Review. *Water Res.* **2021**, *190*, 116723. [CrossRef]
29. Padilla, F.M.; Gallardo, M.; Manzano-Agugliaro, F. Global Trends in Nitrate Leaching Research in the 1960–2017 Period. *Sci. Total Environ.* **2018**, *643*, 400–413. [CrossRef]
30. Petersen, S.O. Greenhouse Gas Emissions from Liquid Dairy Manure: Prediction and Mitigation. *J. Dairy Sci.* **2018**, *101*, 6642–6654. [CrossRef]
31. Zare, L.; Ronaghi, A. Comparison of N Mineralization Rate and Pattern in Different Manure- and Sewage Sludge-Amended Calcareous Soil. *Commun. Soil Sci. Plant Anal.* **2019**, *50*, 559–569. [CrossRef]
32. Gómez-Garrido, M.; Faz-Cano, Á.; Martínez-Martínez, S.; Carmona-Garcés, D.M.; Büyükkiliç-Yanardag, A. Nitrogen Dynamic and Leaching in Calcareous Soils Amended With Pig Slurry. In *Soil Management and Climate Change: Effects on Organic Carbon, Nitrogen Dynamics, and Greenhouse Gas Emissions*; Elsevier Inc.: Amsterdam, The Netherlands, 2018; pp. 171–187, ISBN 9780128121290.
33. Zhang, H.; Hunt, D.E.; Bittman, S. Animal-Based Organic Amendments and Their Potential for Excessive Nitrogen Leaching and Phosphorus Loading. *Agron. J.* **2019**, *111*, 2207–2217. [CrossRef]
34. EC, European Council, (91/676). *Protection of Waters against Pollution Caused by Nitrates from Agricultural Sources*; EC, European Council: Brussels, Belgium, 1991; pp. 1–8.
35. Scott, J.T.; Lambie, S.M.; Stevenson, B.A.; Schipper, L.A.; Parfitt, R.L.; McGill, A.C. Carbon and Nitrogen Leaching under High and Low Phosphate Fertility Pasture with Increasing Nitrogen Inputs. *Agric. Ecosyst. Environ.* **2015**, *202*, 139–147. [CrossRef]
36. Wang, D.; Guo, L.; Zheng, L.; Zhang, Y.; Yang, R.; Li, M.; Ma, F.; Zhang, X.; Li, Y. Effects of Nitrogen Fertilizer and Water Management Practices on Nitrogen Leaching from a Typical Open Field Used for Vegetable Planting in Northern China. *Agric. Water Manag.* **2019**, *213*, 913–921. [CrossRef]
37. Souri, M.K.; Rashidi, M.; Kianmehr, M.H. Effects of Manure-Based Urea Pellets on Growth, Yield, and Nitrate Content in Coriander, Garden Cress, and Parsley Plants. *J. Plant Nutr.* **2018**, *41*, 1405–1413. [CrossRef]
38. Gerke, J. The Acquisition of Phosphate by Higher Plants: Effect of Carboxylate Release by the Roots. A Critical Review. *J. Plant Nutr. Soil Sci.* **2015**, *178*, 351–364. [CrossRef]
39. Tiecher, T.L.; Lourenzi, C.R.; Girotto, E.; Tiecher, T.; De Conti, L.; Marques, A.C.R.; Silva, L.O.S.; Marchezan, C.; Brunetto, G.; Ceretta, C.A. Phosphorus Forms Leached in a Sandy Typic Hapludalf Soil under No-Tillage with Successive Pig Slurry Applications. *Agric. Water Manag.* **2020**, *242*, 106406. [CrossRef]
40. Liu, X.P.; Bi, Q.F.; Qiu, L.L.; Li, K.J.; Yang, X.R.; Lin, X.Y. Increased Risk of Phosphorus and Metal Leaching from Paddy Soils after Excessive Manure Application: Insights from a Mesocosm Study. *Sci. Total Environ.* **2019**, *666*, 778–785. [CrossRef] [PubMed]
41. Ju, X.t.; Zhang, C. Nitrogen Cycling and Environmental Impacts in Upland Agricultural Soils in North China: A Review. *J. Integr. Agric.* **2017**, *16*, 2848–2862. [CrossRef]
42. Wang, Z.; Jiang, H.; Shen, Y. Forage Production and Soil Water Balance in Oat and Common Vetch Sole Crops and Intercrops Cultivated in the Summer-Autumn Fallow Season on the Chinese Loess Plateau. *Eur. J. Agron.* **2020**, *115*, 126042. [CrossRef]

43. Bi, Q.F.; Li, K.J.; Zheng, B.X.; Liu, X.P.; Li, H.Z.; Jin, B.J.; Ding, K.; Yang, X.R.; Lin, X.Y.; Zhu, Y.G. Partial Replacement of Inorganic Phosphorus (P) by Organic Manure Reshapes Phosphate Mobilizing Bacterial Community and Promotes P Bioavailability in a Paddy Soil. *Sci. Total Environ.* **2020**, *703*, 134977. [CrossRef] [PubMed]
44. McDowell, R.W.; Worth, W.; Carrick, S. Evidence for the Leaching of Dissolved Organic Phosphorus to Depth. *Sci. Total Environ.* **2021**, *755*, 142392. [CrossRef] [PubMed]
45. Regueiro, I.; Pociask, M.; Coutinho, J.; Fangueiro, D. Animal Slurry Acidification Affects Particle Size Distribution and Improves Separation Efficiency. *J. Environ. Qual.* **2016**, *45*, 1096. [CrossRef]
46. Kang, J.; Amoozegar, A.; Hesterberg, D.; Osmond, D.L. Phosphorus Leaching in a Sandy Soil as Affected by Organic and Inorganic Fertilizer Sources. *Geoderma* **2011**, *161*, 194–201. [CrossRef]
47. Gichangi, E.M.; Mnkeni, P.N.S.; Brookes, P.C. Effects of Goat Manure and Inorganic Phosphate Addition on Soil Inorganic and Microbial Biomass Phosphorus Fractions under Laboratory Incubation Conditions. *Soil Sci. Plant Nutr.* **2009**, *55*, 764–771. [CrossRef]
48. Manning, D.A.C. How Will Minerals Feed the World in 2050? *Proc. Geol. Assoc.* **2015**, *126*, 14–17. [CrossRef]
49. Ashworth, A.J.; Chastain, J.P.; Moore, P.A. Nutrient Characteristics of Poultry Manure and Litter. In *Animal Manure: Production, Characteristics, Environmental Concerns, and Management*; Waldrip, H.M., Pagliari, P.H., He, Z., Eds.; ASA Special Publications: Clemson, SC, USA, 2020; pp. 63–87, ISBN 9780891183716.
50. Torabian, S.; Farhangi-Abriz, S.; Qin, R.; Noulas, C.; Sathuvalli, V.; Charlton, B.; Loka, D.A. Potassium: A Vital Macronutrient in Potato Production—A Review. *Agronomy* **2021**, *11*, 543. [CrossRef]
51. Macholdt, J.; Piepho, H.P.; Honermeier, B. Mineral NPK and Manure Fertilisation Affecting the Yield Stability of Winter Wheat: Results from a Long-Term Field Experiment. *Eur. J. Agron.* **2019**, *102*, 14–22. [CrossRef]
52. Alfaro, M.A.; Alfaro, M.A.; Jarvis, S.C.; Gregory, P.J. Factors Affecting Potassium Leaching in Different Soils. *Soil Use Manag.* **2004**, *20*, 182–189. [CrossRef]
53. Rowley, M.C.; Grand, S.; Verrecchia, É.P. Calcium-Mediated Stabilisation of Soil Organic Carbon. *Biogeochemistry* **2018**, *137*, 27–49. [CrossRef]
54. Tripolskaja, L.; Baksiene, E.; Razukas, A.; Sidlauskas, G. How Organic Fertilizers Change Chemical Element Leaching: A Summary of the Lysimeter Studies in Lithuania, 1987–2014. *Polish J. Environ. Stud.* **2016**, *25*, 2589–2600. [CrossRef]
55. Wang, Y.; Zhu, Y.; Zhang, S.; Wang, Y. What Could Promote Farmers to Replace Chemical Fertilizers with Organic Fertilizers? *J. Clean. Prod.* **2018**, *199*, 882–890. [CrossRef]
56. de Bang, T.C.; Husted, S.; Laursen, K.H.; Persson, D.P.; Schjoerring, J.K. The Molecular–Physiological Functions of Mineral Macronutrients and Their Consequences for Deficiency Symptoms in Plants. *New Phytol.* **2021**, *229*, 2446–2469. [CrossRef]
57. Pötzsch, F.; Lux, G.; Lewandowska, S.; Schmidtke, K. Field Crops Research Sulphur Demand, Accumulation and Fertilization of *Pisum sativum* L. in Pure and Mixed Stands with *Hordeum vulgare* L. under Field Conditions. *Field Crop. Res.* **2019**, *239*, 47–55. [CrossRef]
58. Prather, R.M.; Castillioni, K.; Kaspari, M.; Souza, L.; Prather, C.M.; Reihart, R.W.; Welti, E.A.R. Micronutrients Enhance Macronutrient Effects in a Meta-Analysis of Grassland Arthropod Abundance. *Glob. Ecol. Biogeogr.* **2020**, *29*, 2273–2288. [CrossRef]
59. Qian, X.Y.; Shen, G.X.; Wang, Z.Q.; Chen, X.H.; Zhao, Q.J.; Bai, Y.J.; Tang, Z.Z. Application of Dairy Manure as Fertilizer in Dry Land in East China: Field Monitoring and Model Estimation of Heavy Metal Accumulation in Surface Soil. *Environ. Sci. Pollut. Res.* **2020**, *27*, 36913–36919. [CrossRef]
60. Sohrt, J.; Lang, F.; Weiler, M. Quantifying Components of the Phosphorus Cycle in Temperate Forests. *WIREs Water* **2017**, *4*, e1243. [CrossRef]
61. Cameselle, C.; Gouveia, S.; Urréjola, S. Benefits of Phytoremediation Amended with DC Electric Field. Application to Soils Contaminated with Heavy Metals. *Chemosphere* **2019**, *229*, 481–488. [CrossRef]
62. Osyczka, P.; Rola, K. Integrity of Lichen Cell Membranes as an Indicator of Heavy-Metal Pollution Levels in Soil. *Ecotoxicol. Environ. Saf.* **2019**, *174*, 26–34. [CrossRef] [PubMed]
63. Seaton, F.M.; Barrett, G.; Burden, A.; Creer, S.; Fitos, E.; Garbutt, A.; Griffiths, R.I.; Henrys, P.; Jones, D.L.; Keenan, P.; et al. Soil Health Cluster Analysis Based on National Monitoring of Soil Indicators. *Eur. J. Soil Sci.* **2021**, *72*, 2414–2429. [CrossRef]
64. Wei, W.; Yang, M.; Liu, Y.; Huang, H.; Ye, C.; Zheng, J.; Guo, C.; Hao, M.; He, X.; Zhu, S. Fertilizer N Application Rate Impacts Plant-Soil Feedback in a Sanqi Production System. *Sci. Total Environ.* **2018**, *633*, 796–807. [CrossRef]