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A step towards the production of manure-based fertilizers: Disclosing the effects of animal species and slurry treatment on their nutrients content and availability

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ABSTRACT

In a context of climate change and circular economy, it is fundamental to produce animal manure-based fertilizers attractive to farmers who are reluctant to use heterogeneous materials, poorly characterized and with unbalanced nutrient contents, namely N:P ratios different from plant requirements. Hence, the aim of the present study was to assess the potential of different treated and non-treated animal manures to produce tailor-made manure-based fertilizers with known N:P ratios. Seven manures were considered: cattle, caprine and poultry solid manures, two contrasting cattle slurries and two contrasting swine slurries. Slurries were further treated by solid-liquid separation, acidification, and acidification followed by solid-liquid separation. Raw and treated manures were fully characterized to assess the effect of manure type and treatment on their nutrient contents and N:P ratios, to incorporate them in manure-based fertilizers with selected N:P ratio. The present results were essential to support the manure-based fertilizer production and identify which materials could be considered: it appears clearly that the pig slurry with all stages of production and the correspondent liquid fraction cannot be used due to their low nutrients content. It was shown that the solid fractions rich in P and with a $N_T:N-NH_4^+$ ratio close to 1 are an excellent material to prepare manure-based fertilizers. Acidification, combined with solidliquid separation, produced a liquid fraction rich in both N and P and with a N_T:P_T ratio close to 1, with the additional benefit of a slow N-release material. Some of the manures or sub-products obtained after treatment provided the usual N:P ratio required by farmers and could be used directly as substitutes of mineral fertilizers. Nevertheless, the blending of some of these materials has a stronger potential to the production of specific manure-based fertilizer.

1. Introduction

Food security for a population in constant growth, with 9.7 billion expected by 2050 (United Nation, 2019), will only be possible with a high degree of specialization and intensification of agriculture and livestock production (Green, 2019). A highly productive agriculture relies on high rates of NPK inputs, mostly from chemical and mineral fertilizers produced from fossil fuels or other non-renewable sources, like phosphate rock (Akram et al., 2019; Eurostat, 2016). On the other hand, livestock production generates a massive amount of organic residues, with 1.4 billion tonnes of animal manure produced per year in 2014, only at the European Union (EU) level (EC, 2014). In fact, manure management became a serious issue in some EU regions, with the intensification and geographical concentration of livestock farms, causing overload production in some areas where the soil available for manure application, at farm scale, might not be enough. It is crucial to develop sustainable nutrient management strategies, not only to ensure food security but, also, to adopt more eco-friendly practices in agricultural systems (Dumont et al., 2019).

The use of manure as a source of macro and micronutrients in agriculture is an ancient practice that, if sustainably performed without over application, can help to solve this nutrients management conundrum: increasing use of fertilizers originated from non-renewable sources in one side and overload production of animal manures on the other (Malomo et al., 2018; Melo et al., 2019). However, manures need to be handled responsibly, i.e., apply the adequate quantity, based on crop nutrient needs, guarantee good storage condition, and perform the correct practices when applying manure. The use of animal manure as

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fertilizer has the potential to reduce i) the environmental impact of the livestock sector, ii) the fertilizing costs to farmers and iii) the dependence on mineral and synthetic fertilizers (He et al., 2016), advantages that could boost this practice to regain the importance that once had. Other important advantages, relative to conventional mineral fertilizers, are the additional supply of micronutrients, important for some crops, and organic matter, with the ability to improve soil health. The manure application to soil in the EU is strictly regulated, considering the environmental risks associated with nitrate diffuse pollution (EC, 1991), and farmers prefer to use mineral fertilizers, not only due to logistic barriers and costs related to raw manure use (e.g., transport, storage, treatment, application), but also because they are reluctant to use materials with a wide range of physical and chemical characteristics and with unbalanced nutrients content (Fangueiro et al., 2018).

The major differences between manures and mineral fertilizers are related to the nutrient's concentration, the nutrients ratios (N:P) and their availability for crops after soil application. Nutrients concentration in manure are much lower than in mineral fertilizers, manures composition vary widely (with animal species, handing practice, bed's composition, storage conditions), their N:P ratios are not similar to the crops needs (Fangueiro et al., 2015; Webb et al., 2010), and a large amount of N and P in manure exists in a non-readily available form for plants (organic fraction). The manure application rate is usually based on the crop's N demand, often resulting in an over-application of P and other elements, with a negative impact on the environment, for instance the accumulation of copper (Cu) and zinc (Zn) in soil top layer that can become toxic to the crops (Popovic et al., 2012).

Some treatments (e.g., slurry acidification, ammonia stripping, solidliquid separation) for animal slurries deliver materials that, directly or combined with others, have the potential to increase their value and acceptance. The solid-liquid separation is a technology that produces a solid fraction with higher dry matter content and richer in nutrients, especially P and N (Hjorth et al., 2010), enabling their transport over longer distances. Another interesting treatment is slurry acidification, a solution that mitigate NH₃ emissions and solubilize P and some micro-nutrients (Fangueiro et al., 2015; ten Hoeve et al., 2016), resulting in a material with a higher value as fertilizer. The animal slurry acidification performed prior to the solid-liquid separation, is also an interesting solution, able to minimize NH₃ emissions during the solid-liquid separation and to increase the P content of the liquid fraction (Cocolo et al., 2016; Regueiro et al., 2016a).

These treatments, that partially increase the nutrients concentrations and plant availability, do not solve the farmers' major problem: there is still a gap between farmers demands in terms of N:P ratio of mineral fertilizers and that provided by available organic fertilizers. The new approach proposed in this study will allow to obtain new organic fertilizers with a known N:P ratio close to what is commonly used by farmers.

Hence, the main objective of the present study was to assess the potential of different treated and non-treated animal manures to produce tailor-made manure-based fertilizers, with selected N:P ratios. For this, manures and slurries from different species were characterized (total macro and micronutrients concentration) and their N:P ratios compared with those commonly found in mineral fertilizers; secondly, some treatments (solid-liquid separation and acidification, by their own or combined) were tested to assess their ability to increase the concentration of some nutrients in their different fractions (solid or liquid), changing their N:P ratios to values closer to commercially available mineral fertilizers. This information will support next stages of the study, where the selected materials will be used in the manure-based fertilizers production, with a specific N:P ratio, and tested to replace, partially or totally, mineral fertilizers in basal fertilization.

2. Material and methods

2.1. Manure sampling

Seven manures, representative of the main Portuguese livestock production systems, were collected in commercial farms: cattle solid manure (CAT) and cattle slurry (BOV+) were collected in an intensive dairy farm (high milk production per cow, milking three times a day, high inputs of concentrated feed) located at Benavente, Portugal. A second cattle slurry (BOV-) was collected in a less intensive dairy farm (lower milk production and concentrated feed inputs) at Palmela, Portugal. The goat manure (GOA) was sampled in an intensive goat farm (indoor production), located at Benavente, Portugal. Two different pig slurries were obtained: one from a farm with all stages of pig production (PSM), located at Águas de Moura, Portugal, and the other from a pig fattening farm (PSF), located at Montijo, Portugal. The poultry manure (POUL) was sampled in a commercial farm dedicated to the production of poultry meat, Herdade Daroeira, at Alvalade-Sado, Portugal.

The raw samples were collected in the main solid manure or slurry store and transported in polyethylene recipients to the lab where they were stored at 4 $^{\circ}$ C before utilization.

2.2. Manure treatments

The raw slurries were submitted to three different treatments solidliquid separation, acidification and combined acidification and solidliquid separation, leading to five derived materials for each slurry.

Slurry acidification was performed by the addition of concentrated sulphuric acid (H_2SO_4 , 98% w/w), to reach a final pH of 5.5 as described in Fangueiro et al. (2009). The amount of acid needed to obtain the target pH varied between 3 and 9 mL kg⁻¹ of slurry.

Slurry solid-liquid separation was performed through centrifugation at 4000 rpm for 7 min in a laboratory centrifuge (5804, Eppendorf, Germany) using 50 mL vials. The 4000 rpm speed is the value established in the lab-scale centrifuge that better simulates the separation performed in the large scale centrifuges used in commercial farms.

The third treatment consisted of a combination of the two previously described treatments: acidification to pH 5.5 followed by the solid-liquid separation by centrifugation at 4000 rpm for 7 min (Fangueiro et al., 2009).

A total of six different materials were then considered for each slurry: i) non-treated slurry (SLU), ii) liquid fraction of SLU (LIQ), iii) solid fraction of SLU (SOL), iv) acidified slurry (A-SLU), v) liquid fraction of A-SLU (A-LIQ), and vi) solid fraction A-SLU (A-SOL).

2.3. Manure physicochemical characterization

All the solid manures, slurries, and the derived materials obtained from the slurry treatment were analysed in triplicate for dry matter content (DM), pH, total organic carbon (TOC), total nitrogen (Total N), ammonium nitrogen (NH_4^+ -N), total phosphorus (Total P, expressed as P_2O_5), total K (expressed as K_2O), and total Ca, Mg and S, as well as for the micronutrients (Fe, Cu, Zn, Mn and B) and Na.

The DM content was determined by drying fresh samples for 24 h at 105 °C in a drying oven (Heraeus Function Line, Thermo Fisher Scientific, USA). The pH of solid manures, SOL and A-SOL were determined in a sample to deionized water suspension (1:10, m/v), after 1 h of occasional agitation, while the pH of SLU, LIQ, A-SLU and A-LIQ was measured directly (Orion 3 Star, Thermo Fisher Scientific, USA). The OM content was determined by calcination of the dried sample for 3 h at 550 °C in a calcination furnace (B180, Naberttherm, Germany) (Clesceri et al., 1989), allowing the total organic carbon (TOC) assessment by dividing the OM content by 1.8 (Sigurnjak et al., 2017). The Total N and NH4⁺-N were measured by the Kjeldahl method (Horneck and Miller, 1998), using the complete procedure (digestion, distillation and titration) for the Total N, and the last two steps for the NH4⁺-N

determination.

Total P, K, Ca, Mg, S, Na and micronutrients were measured after the digestion of an oven-dried sample (\pm 0.2–0.3 g), with 9 mL nitric acid and 3 mL hydrogen peroxide, at 100 °C, in a block digestion system (Digipress MS, SCP Science, Canada). The elements concentrations were determined in the suspensions, using an inductively coupled plasma optical emission spectrometer (iCAP 7000 Series ICP Spectrometer, Thermo Fisher Scientific, America).

2.4. Potential N mineralization assessment

An anaerobic incubation, based on the method described by Fangueiro et al. (2008), was performed to assess the potential N mineralization (PM) of each manure, slurry or derived materials obtained by treatment. A sample amount, equivalent to 0.02 g of total N, was added to 10 g of field-moist soil in a 60 mL syringe, and the total water content was corrected to 25 mL in the soil + manure mixture. The soil used here as inoculum was a sandy soil with an OM content of 7.4 g kg⁻¹ soil. Eight replicates per sample were assembled, and a treatment containing only soil was used as control. Four replicates were prepared in syringes to be incubated for 7 days at 40 °C, while the other half were immediately extracted, after the injection of 25 mL of 4 M KCl to have a final KCl concentration of 2 M and 1:5 (m:V) extraction ratio. The samples were shaken for 1 h, followed by centrifugation at 4000 rpm (Eppendorf 5804), and 10 mL sub-samples of the supernatant were collected and stored at 4 °C before the analysis of the NH₄⁺-N content by segmented flow autoanalyzer SAN plus (San Plus System, Skalar, Nederland) with a modified Berthelot method (Krorn, 1956). The same extraction procedure was used after the 7-days incubation period.

To calculate the PM, the following equation was used (Fangueiro et al., 2008):

 $PM = \{ [NH_4^+ - N]_{post-incub.}(sample) - [NH_4^+ - N]_{pre-incub.}(sample) \} - \{ [NH_4^+ - N]_{post-incub.}(soil) - [NH_4^+ - N]_{pre-incub.}(soil) \}$

All samples were analysed in triplicate and the PM values were expressed as a percentage of the total N mineralized, considering the total N which was used in the incubated sample.

2.5. Statistical analysis of data

Data was analysed by one way ANOVA to evaluate the isolated effect of the manure/slurry species or treatment on the nutrient concentrations. Data were also analysed by two-way ANOVA to assess the effect of the interaction specie x treatment. To define the statistical significance of the mean, a Tukey's test was performed with a 95% degree of confidence ($\alpha = 0.05$), using Statistix 7.

3. Results and discussion

Two scenarios were considered to prepare tailored manure-based fertilizers: i) at a farm level, where the desired N:P ratios and nutrients availability would be obtained by mixing raw or treated manure/slurry from a single animal species, with mineral fertilizers supplementation when needed; and ii) at a centralized plant receiving raw manure/slurry from different animal species, broadening the range of possibilities to blend materials, to obtain the desired manure-based fertilizers.

3.1. Effects of the animal species on the nutrients content and availability

The different animal species considered in the present study produced manure with very distinct chemical and physical characteristics, due not only to their different metabolism and age but also to the type of feeding (Trabue et al., 2019) and bedding material used (Miller et al., 2018). The farm practices, namely manure management techniques, have a marked effect on manure composition that can explain the differences between the results obtained here (Table 1) and those reported by other authors.

Slurries presented lower dry matter content than the solid manures and significant differences were also observed among the slurries and solid manures considered (Table 1). The slurries DM ranged between \sim 20 g kg⁻¹, for PSM, and \sim 120 g kg⁻¹ for PSF. The differences were even higher when comparing slurry and solid manure, for instance, \sim 740 g kg⁻¹ for POUL. That is one of the main constraints of using slurry as fertilizer, when comparing with solid manure: the lower DM content of slurry (Table 1) implies a higher dilution of nutrients and the handling of a significantly higher amount of slurry to provide the same amount of nutrients. This point is the main limitation for a massive use of slurry as organic fertilizers in arable crops, since transport and soil application of manure will be much more expensive compared to mineral fertilizer. On the opposite, the higher DM of the solid manure can affect strongly soil application with potential clogging of the equipment and lead to a heterogeneous application. A tailor-made fertilizer would bring the benefit of using both solid manure and slurries to reach a compromise between a material extremely diluted or too solid, being one of the aspects to take into account when planning to produce a manure-base fertilizer.

More than a nutrient supplier, solid manures are an excellent source of carbon (C). The solid manures presented the higher organic C concentration (in a fresh material basis), with \sim 342 g kg⁻¹, 112 g kg⁻¹ and \sim 85 g kg⁻¹, for POUL, GOA, and CAT, respectively (Table 1). Slurries also provide interesting amounts of C to the soil, but with lower concentrations than manures and with significant differences between products, for instance, 10.03 and 55.22 g C kg^{-1} in PSM and PSF, respectively. To provide the same amount of C to the soil, the quantity of PSM needed is five times higher than the PSF. It is well known that there is a positive correlation between the C content of organic amendments and their capacity to restore the soil organic matter (SOM) (FAO, 2019), indicating that the use of manures as organic fertilizers may be a good option to improve soil's health. The Mediterranean soils have either a low (<2%) or very low (<1%) SOM content, a fact that needs to be counterbalanced by the application of exogenous sources of OM to soil (Hinsinger, 2014).

Besides the rich C content of solid manures, these materials had also higher or similar N, P and K content relative to slurries, but lower than mineral fertilizers, which might limit their use as a nutrient supplier and highlight them instead as interesting C providers (i.e., organic amendments), becoming essential to produce a manure-based fertilizer with a higher nutrient concentration and known N:P ratio. Some nutrients in solid manures are mostly in forms not readily available for plants, which might be seen as a drawback, if an immediate plant availability is foreseen, or as an important advantage, if a slower nutrient release is expected (as occurs in the slow-releasing mineral fertilizers). Both goat and cattle manure had higher total N content but lower NH4⁺-N content than both cattle slurries and pig fattening slurry (Table 1), resulting in a lower N availability to the crops immediately after soil application (low NH₄⁺: total N ratio), but providing a longer lasting N supply to the crops, extended over time. From the three solid manures, poultry manure appears as the most interesting when an extra source of N is needed since it has the highest DM, total N and NH₄⁺-N content (Table 1).

The values of pH ranged from 6.69 to 9.04, with significant differences among animal species with the lower value for the pig slurry from the fattening farm and the higher for the poultry manure. The higher pH of cattle slurry (intensive farm), goat and poultry manure can be utilized to correct or increase the pH in acidic soils (Cai et al., 2018). Nonetheless, a higher pH in manure, especially with a pH between 7 and 10, increase the risk of ammonia emissions (Ndegwa et al., 2008), so the referred materials should be blended with materials with lower pH or even treated by acidification (Fangueiro et al., 2015).

The values of potential N mineralization (PM) indicated that poultry manure is the material with the higher mineralization rate (PM \sim 23% of

Table 1

Physicochemical characteristics of the raw manures from the animal species considered in the study, all expressed in fresh matter basis (mean value, n=3). Valu	ues in
the same column followed by the same letter are not statistically different (Tukey HSD test, $P > 0.05$).	

	DM g kg ⁻¹	рН	TOC g kg ⁻¹	Total N g N kg ⁻¹	NH4 ⁺ -N g N kg ⁻¹	PM % of total N	Total P g P ₂ O ₅ kg ⁻¹	Total K g K ₂ O kg ⁻¹	Total Ca g kg ⁻¹	Total Mg g kg ⁻¹	Total S g kg ⁻¹
BOV+	71.64 ^f	8.55 ^b	24.24^{f}	3.10 ^c	1.70 ^c	13.41 ^b	1.32 ^d	4.98 ^b	1.08 ^{de}	0.62 ^d	0.01 ^{cd}
BOV-	97.78 ^e	7.13 ^e	40.09 ^e	3.53 ^c	1.65^{b}	11.81 ^{bc}	1.62^{d}	3.21 ^{bc}	1.37 ^{de}	0.57^{d}	1.37^{a}
PSM	22.85 ^g	7.19 ^e	10.03 ^g	1.31^{d}	0.74 ^e	12.75^{bc}	0.68 ^e	0.59^{d}	0.54 ^e	0.27^{e}	0.00^{d}
PSF	124.12 ^d	6.69 ^f	55.22 ^d	6.16^{b}	3.71^{a}	7.99 ^d	3.74^{b}	4.71 ^b	2.61 ^c	1.27^{c}	0.96 ^b
CAT	176.79 ^c	7.77 ^d	85.43 ^c	3.14 ^c	0.44 ^f	11.07 ^c	3.54 ^b	1.88^{cd}	2.02^{cd}	1.38 ^c	0.01 ^{cd}
GOA	244.00^{b}	8.09 ^c	112.18^{b}	5.06 ^b	0.90^{d}	8.02 ^d	2.66 ^c	0.82^{cd}	7.84 ^b	2.01^{b}	0.01 ^{cd}
POUL	739.88 ^a	9.04 ^a	342.32 ^a	21.41 ^a	3.14^{b}	22.56 ^a	11.71 ^a	19.71 ^a	11.79 ^a	4.80 ^a	0.10 ^c

Bov+: Intensive cattle slurry; Bov- : Cattle slurry; PSM: Pig slurry with all stages of pig production; PSF: Pig slurry from a fattening farm; CAT: Cattle manure; GOA: Goat manure; POUL: Poultry manure. DM: Dry matter; TOC: Total organic carbon; Total N: Total nitrogen; NH₄⁺-N: Ammoniacal nitrogen; PM: Potential of mineralization; Total P: Total phosphorus expressed as P₂O₅; K: Total potassium expressed as K₂O; Ca: Total calcium; Mg: Total magnesium; S: Total sulphur.

total N), which suggests that, besides the higher content of immediately available N (NH4⁺-N), a significant part of the organic N should be quickly mineralized, allowing a significant N uptake by the plants (Table 1). The same cannot be said relatively to cattle and goat manures, which had lower PM values, $\sim 11\%$ and 8% of the total N, respectively, in the same range of the slurries' PM values, indicating that the organic N from these two manures will be slowly mineralized. The low PM values of these manures might be a consequence of their richness in recalcitrant materials, like straws and parings, elements rich in fibres, leading to higher C:N ratios and, consequently, to less labile nutrients (Vahdat et al., 2011). Accordingly, the slurries with more plant residues (e.g., bedding materials), namely cattle slurries, should have presented the lower PMs. No major differences were observed for the PM of the slurries, except for the PSF, the slurry with the lower PM value and the higher total N content. PSF presented a PM value corresponding to $\sim 8\%$ of the total N applied, identical to GOA, which may be attributed to the bigger particles size existing in PSF, compared to the other three slurries. Fangueiro et al. (2012) reported similar results with different slurries and attributed it to the fact that bigger particle size in slurry turned the total N less soluble and, therefore, the N mineralization was slowed down, a feature that can be considered important in a manure-based fertilizer able to slowly supply N to the plant.

The poultry manure presented a P concentration ~ three, ~four and 10 times higher than GOA, CAT and PSF, and both cattle slurry and PSM, respectively (Table 1). This can be an important material to add to a blend for a crop with higher P needs. The P content of POUL (~12 g P kg^{-1}) is coherent with the value of 13 g P kg^{-1} reported by Adekiya et al. (2019), similar to that of Shah et al. (2016), which reported values of P_2O_5 between 14.1 and 19 g kg⁻¹ DM in a solid cattle manure, values higher than those observed here in fresh manures, perhaps due to the higher maturity and DM content of the manure referred by these authors. The slurry from the pig fattening farm, had the higher total P content (~5.5 times higher than the value of the other pig slurry, and almost the double P of the cattle slurries). On the opposite side, PSM presented the lower P concentration followed by both cattle slurries. This aspect is important when a blend richer in N is needed or when it is necessary to apply a poor-P material to a soil with a high P concentration.

Regarding total K, it is noteworthy the high content present in POUL and in the slurries BOV+ and PSF, indicating their ability to provide this essential macronutrient to the crop (Table 1). The differences observed within each species, which are very marked in the case of total K concentrations in PSM and PSF, might be attributed to distinct animal dieting programs. It is still to refer that the poultry manure appears also as an optimal material to supply both Ca and Mg while, in the case of slurries, the best option to provide Ca and Mg is PSF. BOV- is as well an excellent source of S, a nutrient essential for many crops and that starts to be in deficit in some European soils (Pötzsch et al., 2019; Scherer, 2009).

3.2. Effects of slurry treatment on nutrients content and N availability

One of the hypotheses considered to obtain manure-based materials with more interesting fertilizer characteristics was to submit the raw materials to pre-treatments, to deliver new products with a composition more adjusted to the nutritional needs of the main crops, namely a higher concentration of some specific elements or higher nutrients availability. The application of these pre-treatments is very important for slurries, which have lower DM content, in this case BOV+, BOV-, PSM and PSF. The treatments which were applied, i) solid-liquid separation, ii) acidification, and iii) acidification followed by solid-liquid separation, were chosen considering their common use at farm scale (separation) (Dennehy et al., 2017), and their potential to minimize ammonia emissions (acidification) (Fangueiro et al., 2015).

3.2.1. Solid-liquid separation

The solid-liquid separation was first introduced to lower the costs and efficiency of slurry management, allowing the transport of a concentrated solid fraction from regions with overproduction of manure to other regions with nutrient deficiency (Fangueiro et al., 2011). Sommer et al. (2015) also emphasized that, since manure application rates are based firstly on N, the over-application of P can be avoided with this strategy. The liquid fraction is, usually, richer in N and K, which becomes an optimal solution to their application directly at the farm, while the solid fraction, with a higher content of organic matter and P, can be exported to a different area. This technique only modifies the nutrients ratios within each phase, solid or liquid, it does not completely remove P from the liquid fraction, only allows the reduction of P concentration in this fraction.

The impact of the separation on the solid and the liquid fractions, in terms of their physicochemical characteristics, were similar for all slurries (Table 2). Solid-liquid separation led to solid fractions (SOL) with pH values higher than the respective liquid fractions (LIQ) (Table 2), in agreement with other studies (Fournel et al., 2019; Gómez-Muñoz et al., 2016). In terms of total N, the LIQ fractions presented lower concentrations, comparatively to SLU and SOL, due to the removal of a significant part of the organic matter. However, the concentration of NH4⁺-N did not differ significantly between the fractions and the untreated materials, in the case of the cattle slurries, while for the pig slurries SOL presented a higher concentration of NH4⁺-N. But it is to note that \sim 72% of the total N was in the form of NH₄⁺-N, in the case of the LIQ of BOV+, BOV- and PSF, and \sim 83% for PSM, against \sim 40% in the SOL of BOV+, BOV- and PSF and \sim 22% in the SOL of the PSF. This can be an important factor to consider when designing a manure-based fertilizer with higher quantities of available N (higher N:P ratio). Similar results were reported by Fangueiro et al. (2009), who obtained a liquid fraction from pig slurry poor in organic N. No significant differences were found between PM values of solid and liquid fractions obtained from cattle slurry but, when considering pig slurry, significantly higher values of PM were found in the SOL than in LIQ fractions (Table 2). Table 2

Physicochemical characteristics of the materials obtained from the treated slurries, expressed in fresh matter basis (mean value, n=3). Values in the same column followed by the same letter are not statistically different (Tukey HSD test, P > 0.05).

		DM g kg ⁻¹	pН	TOC g kg ⁻¹	Total N g N kg ⁻¹	NH4 ⁺ -N g N kg ⁻¹	PM % of total N	Total P g P ₂ O ₅ kg ⁻¹	Total K g K ₂ O kg ⁻¹	Total Ca g kg ⁻¹	Total Mg g kg ⁻¹	Total S g kg ⁻¹
BOV+	SLU LIQ SOL A-SLU A-LIQ A-SOL	$71.64^{i} \\ 37.54^{jkl} \\ 159.96^{d} \\ 76.71^{i} \\ 45.61^{j} \\ 137.49^{ef}$	8.55 ^{bc} 7.45 ^e 8.84 ^a 4.97 ^q 5.04 ^{pq} 5.10 ^{op}	$24.24^{i} \\ 12.50^{k} \\ 54.85^{ef} \\ 25.21^{i} \\ 12.53^{k} \\ 49.46^{fg}$	3.10^{hi} 2.70^{ij} 4.70^{f} 3.15^{hi} 2.89^{i} 4.16^{g}	1.70^{e} 1.97^{de} 1.85^{de} 1.86^{de} 1.76^{de}	13.41^{efg} 11.66 ^g 12.08 ^{fg} 7.05 ^{hi} 5.11 ^{lj} 14.66 ^{def}	$1.32^{\rm h} \\ 0.43^{\rm ij} \\ 4.02^{\rm c} \\ 1.48^{\rm gh} \\ 1.46^{\rm gh} \\ 1.36^{\rm h}$	4.98^{a} 1.81^{cde} 1.79^{e} 1.89^{cde} 1.89^{cde} 1.48^{f}	$1.08^{\rm fg} \\ 0.64^{\rm hi} \\ 2.59^{\rm c} \\ 1.30^{\rm fg} \\ 1.04^{\rm fg} \\ 1.24^{\rm fg}$	$\begin{array}{c} 0.62^{\rm fg} \\ 0.37^{\rm hi} \\ 1.62^{\rm b} \\ 0.69^{\rm efg} \\ 0.70^{\rm ef} \\ 0.57^{\rm fgh} \end{array}$	$\begin{array}{c} 0.01^{j} \\ 0.21^{ij} \\ 0.61^{hi} \\ 4.14^{d} \\ 3.98^{de} \\ 3.67^{a} \end{array}$
BOV-	SLU LIQ SOL A-SLU A-LIQ A-SOL	$\begin{array}{r} 97.78^{h} \\ 25.92^{klm} \\ 150.48^{de} \\ 99.98^{h} \\ 39.54^{jk} \\ 192.62^{c} \end{array}$	$7.13^{f} \\ 8.53^{v} \\ 8.82^{a} \\ 5.81^{j} \\ 5.92^{i} \\ 6.45^{h}$	$\begin{array}{c} 40.09^{h} \\ 8.89^{k} \\ 56.67^{e} \\ 37.83^{h} \\ 12.50^{k} \\ 76.76^{c} \end{array}$	$\begin{array}{c} 3.53^{h} \\ 2.32^{j} \\ 4.73^{f} \\ 3.45^{h} \\ 2.70^{ij} \\ 4.79^{f} \end{array}$	1.65^{e} 1.66^{e} 1.87^{de} 1.72^{de} 1.74^{de} 1.76^{de}	$11.81^{g} \\ 18.97^{bc} \\ 17.41^{cd} \\ 7.19^{hi} \\ 3.88^{j} \\ 4.66^{ij}$	$\begin{array}{c} 1.62^{\rm fgh} \\ 0.53^{\rm ij} \\ 3.12^{\rm d} \\ 1.85^{\rm fg} \\ 1.71^{\rm fgh} \\ 2.37^{\rm e} \end{array}$	$\begin{array}{r} 3.21^{b} \\ 0.91^{g} \\ 0.86^{gh} \\ 0.87^{gh} \\ 0.95^{g} \\ 0.96^{g} \end{array}$	$\begin{array}{c} 1.37^{\rm ef} \\ 0.57^{\rm i} \\ 1.93^{\rm d} \\ 1.24^{\rm fg} \\ 0.97^{\rm gh} \\ 1.92^{\rm d} \end{array}$	$\begin{array}{c} 0.56^{\rm fgh} \\ 0.25^{\rm ij} \\ 0.82^{\rm e} \\ 0.51^{\rm gh} \\ 0.53^{\rm fgh} \\ 0.65^{\rm efg} \end{array}$	
PSM	SLU LIQ SOL A-SLU A-LIQ A-SOL	22.85 ^{lmn} 4.50 [°] 156.95 ^d 19.20 ^{mno} 9.00 ^{no} 134.59 ^f	$7.19^{f} \\ 7.14^{f} \\ 7.82^{d} \\ 5.19^{no} \\ 5.67^{k} \\ 5.16^{no}$	$10.03^{k} \\ 1.49^{m} \\ 68.98^{d} \\ 7.46^{kl} \\ 2.62^{lm} \\ 63.98^{d}$	$\begin{array}{c} 1.31^k \\ 0.80^l \\ 6.35^{cd} \\ 1.09^{kl} \\ 0.80^l \\ 4.51^{fg} \end{array}$	$\begin{array}{c} 0.74^{\rm g} \\ 0.66^{\rm g} \\ 1.37^{\rm f} \\ 0.74^{\rm g} \\ 0.71^{\rm g} \\ 1.18^{\rm f} \end{array}$	$12.76^{fg} \\ 3.36^{j} \\ 27.54^{a} \\ -3.13^{m} \\ -8.39^{n} \\ 7.37^{hi} \\ \end{cases}$	$egin{array}{c} 0.68^{ij} \\ 0.26^{j} \\ 4.62^{b} \\ 0.79^{i} \\ 0.71^{ij} \\ 1.99^{ef} \end{array}$	0.59^{hi} 0.26^{j} 0.43^{ij} 0.26^{j} 0.29^{ij} 0.33^{ij}	$\begin{array}{r} 0.54^{i} \\ 0.10^{j} \\ 4.18^{b} \\ 0.54^{i} \\ 0.45^{ij} \\ 1.73^{de} \end{array}$	$\begin{array}{c} 0.27^{ij} \\ 0.10^{j} \\ 1.74^{b} \\ 0.25^{ij} \\ 0.21^{ij} \\ 1.05^{d} \end{array}$	$\begin{array}{c} 0.00^{\rm j} \\ 0.03^{\rm j} \\ 0.80^{\rm h} \\ 0.93^{\rm gh} \\ 0.93^{\rm gh} \\ 1.63^{\rm f} \end{array}$
PSF	SLU LIQ SOL A-SLU A-LIQ A-SOL	$\begin{array}{r} \hline 124.12^{\rm fg} \\ 46.18^{\rm j} \\ 232.04^{\rm a} \\ 117.63^{\rm g} \\ 62.62^{\rm i} \\ 210.59^{\rm b} \end{array}$	$\begin{array}{r} 6.69^{\rm g} \\ 7.48^{\rm e} \\ 8.62^{\rm b} \\ 5.21^{\rm n} \\ 5.41^{\rm l} \\ 5.31^{\rm m} \end{array}$	55.22 ^e 18.01 ^j 107.63 ^a 48.95 ^g 20.57 ^{ij} 98.15 ^b	6.16 ^{cd} 5.51 ^e 9.87 ^a 6.58 ^c 6.07 ^d 7.77 ^b	$3.71^{c} \\ 4.06^{ab} \\ 4.26^{a} \\ 4.20^{a} \\ 4.24^{a} \\ 3.92^{bc}$	$7.99^{h} \\ 15.59^{de} \\ 20.44^{b} \\ 4.72^{lj} \\ 0.69^{l} \\ 6.30^{hij}$	$\begin{array}{r} 3.74^{c} \\ 0.78^{i} \\ 11.03^{a} \\ 4.08^{c} \\ 4.16^{bc} \\ 3.88^{c} \end{array}$	$\begin{array}{r} 4.71^{a} \\ 1.76^{ef} \\ 2.09^{cd} \\ 2.03^{cde} \\ 2.10^{c} \\ 1.80^{de} \end{array}$	$2.61^{c} \\ 1.18^{fg} \\ 5.86^{a} \\ 2.80^{c} \\ 1.84^{d} \\ 4.08^{b}$	$\begin{array}{r} 1.27^{\rm c} \\ 0.26^{\rm ij} \\ 3.44^{\rm a} \\ 1.37^{\rm c} \\ 1.36^{\rm c} \\ 1.27^{\rm c} \end{array}$	$\begin{array}{r} 0.96^{\mathrm{gh}} \\ 0.49^{\mathrm{hij}} \\ 1.44^{\mathrm{fg}} \\ 5.49^{\mathrm{b}} \\ 4.69^{\mathrm{c}} \\ 6.15^{\mathrm{a}} \end{array}$

Bov+: Intensive cattle slurry; Bov-: Cattle slurry; PSM: Pig slurry with all stages of pig production; PSF: Pig slurry from fattening farm. SLU: Non-treated slurry; LIQ: Liquid fraction; SOL: Solid fraction; A-SLU: acidified slurry; A-LIQ: Liquid fraction of the acidified slurry; A-SOL: Solid fraction of the acidified slurry; DM: Dry matter;; TOC: Total organic carbon; Total N: Total nitrogen; NH₄⁺-N: Ammoniacal nitrogen; PM: Potential of mineralization; Total P: Total phosphorus expressed as P₂O₅; K: Total potassium expressed as K₂O; Ca: Total calcium; Mg: Total magnesium; S: Total sulphur.

These results are in contrast with those reported by Regueiro et al. (2016a), who did not observe significant differences in PM values between fractions derived from pig slurry. The reason for such difference is not clear and might be related to the particle size or C speciation existing between pig and cattle slurry since the SOL and LIQ fractions derived from pig and cattle slurry had a similar C:N ratio.

The use of solid-liquid separation resulted in solid fractions not only richer in organic C content, but also richer in P, as already referred by Sommer et al. (2017). All solid fractions, independently of being obtained from cattle or pig slurries, presented a higher total P content. However, for pig slurries, the P concentrations obtained here were slightly lower than the values presented by Regueiro et al. (2016c) in a study to evaluate the behaviour of nutrient distribution with the treatments applied. The solid fractions obtained in this study were an optimal solution to supply larger amounts of P and, also, to provide Ca and Mg and, thereby, obtain a manure-based fertilizer with a lower N:P ratio.

When considering the possibility of using a subproduct of the solidliquid separation to produce manure-based fertilizers, SOL is the best option to simultaneously provide P and C to the soil. Also, solid fractions derived from PSM and PSF presented the higher PM, an important factor when the intention is to obtain a blend rich in readily available N. However, the high Cu and Zn content of these fractions might be problematic (Table 2S from supplementary material). Popovic et al. (2012), have already alerted for the enrichment of the solid fractions with Cu and Zn, and the concomitant risk of soil toxicity and impaired crop productivity. The liquid fractions, with lower N content than the solid fractions, have a higher proportion of available N, which might be a good option to enrich some blends in available N (higher N:P ratio).

Despite the benefits that may arise from the slurry solid-liquid separation, the process might lead to NH_3 emissions during the treatment and, individually, the fractions can still release, during the storage period, larger amounts of NH_3 and greenhouse gases emissions (GHG) than raw slurries, decreasing their fertilizer value (Regueiro et al., 2016c). That is why it is also important to consider the slurry

acidification.

3.2.2. Acidification

Slurry acidification appears as a mitigation technique to reduce not only NH₃ but also GHG emissions during storage (Prado et al., 2020). It is applied at farm scale in several countries from the North and East Europe, and also started to be implemented in countries from other European regions, like in Spain (Rodhe et al., 2018). The additives used for acidification are known to have an impact on the characteristics of the acidified slurry (Regueiro et al., 2016b) but it was not possible to test several additives in the present study. Sulphuric acid was selected for being the most used and, also a source of sulphur (S). By using this technique, N losses by NH₃ volatilization are minimized and, consequently, the slurry fertilizer value, in terms of N, is increased. Additionally, P becomes more soluble, which could result in a higher availability of this element to the crop (Pedersen et al., 2017; Roboredo et al., 2012). This technique can be used to obtain a higher N:P ratio, due to the increase in N fertilize value and P solubility. Nevertheless, the safety issues related to acid handling and associated cost might be a limitation to the applicability of acidification at the farm level (Fangueiro et al., 2015).

In terms of TOC concentration, there were no differences between acidified and raw slurries, as expected, despite the inorganic C losses through CO_2 emissions that may occur during treatment by acidification (Fangueiro et al., 2013).

The total N and NH_4^+ -N contents were similar in the raw and the respective acidified slurries, as observed by other authors (Fangueiro et al., 2009; Regueiro et al., 2016a). Such results were expected since the storage time of the materials was very short, leading to residual NH_3 losses from the untreated slurries, or to no emissions at all. Previous studies indicated that slurry acidification alters the N dynamic after soil application, inhibiting or delaying the nitrification and decreasing the N mineralization (Fangueiro et al., 2017; Sigurnjak et al., 2017). This effect was evident in the results, with a significantly lower value of PM in

the A-SLU fractions, relatively to the non-treated slurries, namely in the PSM where the PM value of the A-SLU was four times lower than in SLU (Table 2). As observed in the present study, Regueiro et al. (2016a) also reported that despite their similar total N and $\rm NH_4^+-N$ contents, the PM values of acidified materials are minor than their non-acidified counterparts.

When using an acidified slurry with other raw or treated manures to produce a manure-based fertilizer, a fraction of the N in the resulting blend will not be available immediately, acting as a slow-release N fertilizer.

As found for N, acidification did not alter the total P concentration comparing the raw slurries and their acidified equivalents. However, acidification is known to solubilize P and, thereby, may increase P availability to crops (Regueiro et al., 2016a; Roboredo et al., 2012), but this aspect was not assessed in the present experiment.

The additive used, sulphuric acid, led to an increase in the S concentration in the acidified slurries, comparatively to their respective raw slurries (Table 2). This can be seen as an advantage when the crops' fertilization plan demands for a S supply. However, it may be problematic when considering the hydrogen sulfate emissions since the addition of inorganic sulphur stimulates the sulfate-reducing bacteria activity (Dai and Blanes-Vidal, 2013). Nevertheless, different acidifying agents might be used as an alternative to sulphuric acid to avoid such problem (Prado et al., 2020; Regueiro et al., 2016b).

3.2.3. Acidification followed by solid-liquid separation

Solid-liquid separation after acidification was considered by Fangueiro et al. (2009) and Regueiro et al. (2016a) as an important strategy to mitigate the N losses from NH3 volatilization and to increase the fertilizer value of the acidified liquid fractions (A-LIQ) by enriching them in P, Ca, Mg and S, in agreement with the results obtained in this study (Table 2). However, this treatment had no effect on both total and mineral N content, or the effect was very reduced. Similarly to what was observed for the acidified slurries, the PM values of the obtained fractions, A-LIQ and A-SOL, were lower than in their respective non-acidified counterparts, LIQ and SOL. Gómez-Muñoz et al. (2016) used fattening pig slurry to assess the potential of N mineralization with fresh and acidified slurry and their solid and liquid fractions, with and without acidification and observed that the solid fraction presented higher PM than the correspondent acidified solid fraction, obtained using centrifugation. Acidification with sulphuric acid turns both A-LIQ and A-SOL a source of S, relatively to their non-acidified fractions. Furthermore, the A-LIQs were richer in total P when compared to the respective liquid fractions (~3.4 times richer in cattle slurries, ~2.7 times richer in PSM and ~5 times richer in PSF). Accordingly, the obtained acidified solid fractions were poorer in P than the respective solid fractions (~3 times in BOV+ and PSF, ~2.3 times in PSM and 1.31 times in BOV-). The results obtained here for total and mineral N, as well as for total P, were in agreement with those obtained by Fangueiro et al. (2017) with cattle slurry. The materials obtained by the combination of solid-liquid separation and acidification were distinct than those obtained only by solid-liquid separation, which may lead to different N:P ratios and different N and P availabilities.

3.3. Potential of manures and slurries to be used in manure-based fertilizers

Some of the manures considered in this study and discussed in subchapter 3.1 showed a strong potential to be used in manure-based fertilizers. PSF presented the highest DM content of all the slurries, the highest concentration of mineral N of all the materials (3.71 g NH_4^+ -N kg⁻¹), and the lowest PM of all slurries, with a high total N content (6.16 g kg^{-1}). This makes PSF one of the best options to provide high inputs of available N with an extra N amount that will be slowly released to the crop (higher N:P ratio). On the other hand, POUL may supply both N and P, and it may be an option to supply N more quickly to the crop, due to the higher PM, with the benefit of adding a considerable amount of C to the soil. When considering Ca and Mg concentrations (Table 1), as well as Cu, Zn, and B (Supplementary Material, Table S1), PSF and POUL were the slurry and the manure, respectively, with the higher concentrations for those important nutrients, meaning that, when used in a manure-based fertilizer, besides the N and P, also essential macro and micronutrient will be provided. Cattle manure presented a lower concentration of mineral N, but a higher concentration of total P, turning this material valuable to provide a manure-based fertilizer rich in P (lower N:P ratio).

Nutrient's concentrations and N availability in the manures were evaluated within each species or derived materials obtained by submitting the slurries to low-technological treatments, i.e., at a farm level scenario. Nevertheless, blends might also be prepared at manure treatment plants, receiving several types of manures, and applying distinct treatments. In this study, it was hypothesized that the nutrient ratios would be used as an indicator to prepare blends of raw or treated manures from different species at a treatment-plant level. In this sense, different N, P and C ratios were calculated for all the manures and raw/ treated slurries (Fig. 1): i) total N to total P ratio (N_T : P_T ratio), ii) NH_4^+ -N to total P ratio (NH4+-N: PT ratio), iii) total N to NH4+-N ratio (NT:NH4+ ratio) and iv) TOC to total N ratio (Corg:N ratio). These indicators will allow identifying the materials with greater ability to provide organic C to soil, materials richer in N or P, with higher or lower N:P ratio, as well as those with lower or faster nutrients release. This information will support the choice of materials to be used for the preparation of manurebased fertilizer with a known ratio of N:P. In all these ratios, P was expressed as P2O5 as occurs in mineral fertilizers.

The manures and raw/treated slurries were presented in Fig. 1A in ascending order of $N_T:P_T$ ratio. This layout emphasizes the materials which are richer in total P (lower N:P ratio), relatively to their N content (in the left side of the graph), and those which are richer in total N, relatively to their P content (in the right side of the graph), allowing their selection considering the crops demands, giving important information to be used in the preparation of the tailored made fertilizers. The same order for the materials was used in the following graphs (Fig. 1B, C and 1D), to facilitate the comparison.

The materials with the lower total P concentrations, like the slurry liquid fractions and the acidified solid fractions, were those with the higher N_T:P_T ratios (Fig. 1A). This effect was more noticeable in PSM LIQ and BOV + LIQ. Contrariwise, the materials with the lower total N concentrations, like the CAT and the solid fraction of PSF, were those with the lower N_T/P_T ratios. To prepare a manure-based fertilizer with materials with the higher N_T:P_T ratios, like the previously referred, it is important to mix them with contrasting materials with a lower ratio when the intention is to have a more balanced ratio, as PSF SOL, that have a higher P concentration. When considering NH_4^+ -N: P_T ratio (Fig. 1B), all the SOLs and solid manures presented the lower ratios, indicating a higher concentration of total P. This is an important indicator since it considers the readily available N and, in the case of the slurry solid fractions and solid manures, it means that they will supply a higher amount of P for the same amount of N applied. It is also to note that the A-SLU and SLU presented an NH_4^+ -N: P_T ratio close to 1, meaning that, with these materials, NH4⁺-N and total P will be supplied in similar quantities, which can be a good solution for basal applications (pre-planting or pre-sowing) but should be used with cautious afterwards, to avoid the surplus application of P.

Considering the $N_T:NH_4^+$ ratio (Fig. 1C), as expected, the solid manures (CAT, GOA and POUL) that presented a higher concentration of organic N, presented the highest $N_T:NH_4^+$ ratio. It is also to note that, the ratios presented by the LIQ fractions were only slightly above 1, highlighting a balance between total and mineral N, which can indicate that these materials can be a good option when more readily available N is needed. Data plotted in Fig. 1A and B can also be used to identify if the N is readily available (lower ratios) or will be slowly released in the medium or long term (higher ratios), an important information to be used



Fig. 1. Main ratios of C, N and P in the materials considered in the study. (A) $N_T:P_T$, the ratio of total N to total P (as P_2O_5); (B) NH_4^+ -N: P_T , the ratio of total N to NH_4^+ -N: P_T , the ratio of total N to total P (as P_2O_5); (C) $N_T:NH_4^+$ -N, the ratio of total N to NH_4^+ -N; and (D) C: N_T , the ratio of C to the total N. Bov+: Intensive Cattle Slurry; Bov-: Cattle Slurry; PSM: Pig Slurry with all stages of pig production; PSF: Pig Slurry from fattening farm; CAT: Cattle Manure; Goa: Goat Manure; POUL: Poultry Manure. LIQ: Liquid Fraction; SOL: Solid Fraction; ACID: Acidified Slurry; A-LIQ: Liquid Fraction of the Acidified Slurry; A-SOL: Solid Fraction of the Acidified Slurry.

in the design of crop-tailored fertilizers from the blend of raw or treated manures.

Another important aspect, that affects mainly the N availability after soil application, is the C:N_T ratio (Fig. 1D). As expected the materials which presented the higher C:N_T ratio were the solid manures, CAT, GOA and POUL, with ratios of 27, 22 and 16, respectively. These materials were those with the higher N_T:NH₄⁺-N, due to the higher content of organic materials like straws and parings (Vahdat et al., 2011), poorer in mineral N (plant available form), as a result of the presence of recalcitrant materials that may inhibit/delay the activity of bacteria responsible for N mineralization. However, this effect was reflected on PM only in the case of GOA, which presented the lower PM rates. This fact can be explained by the C:N_T ratios, which were not at a critical level that would result in a more marked effect on the mineralization.

Another challenge is to use the information provided by these ratios and design possible manure-based blendings. One specific application, regarding the centralized solution at a treatment plant, could be the blending of PSM, which has a higher concentration of N_T , NH_4^+ -N and P, with BOV+, the one richest in K. Also, both slurries have a high, or medium, PM value, reason why it would be interesting to blend them with a material with a lower PM, or higher $N_T:NH_4^+$ ratio, indicating a higher quantity of organic N, and a lower mineralization rate (e.g., an acidified slurry). This should guarantee a continuous N supply to the crop, besides the mineral N initially available and, also, the capacity to increase soil nutrients and the C pool, important to enhance the soil's health.

Considering the formulation of blends at the farm scale, one important material to be used should be the PSF slurry, due to its high concentrations in both total and mineral N, and considerable high concentrations for P and K, which will be a good contender for a manure-based fertilizer with an even ratio of N:P. Moreover, the materials

obtained from the application of the tested treatments to PSF slurry were those richer in most of the parameters evaluated.

To be able to evaluate the potential of each material to be used in the production of manure-based fertilizers, some calculations were made (Table 3) taking as a reference the provision of 100 kg N ha⁻¹ to the soil (first column), and further calculating (i) the quantity of manure or slurry (raw or treated) needed to provide the referred 100 kg N ha⁻¹ (second column), (ii) the estimated available N content (Nav) (third column), (iii) the Nav:P2O5:K2O ratios (fourth column), (iv) the amount of macronutrients provided to the crop by the application of that quantity of manure (P2O5, K2O, Mg, Ca and S), and (v) the amount of organic C provided by that application (last column, Table 3). To estimate the available N content (Nav; i.e., mineral N + organic N that can, potentially, be mineralized), the Portuguese legislation was considered where: 50% of the total N is considered as available N in solid manures (CAT, GOA and POUL), and in solid fractions obtained by solid-liquid separation (SOL and A-SOL), while, approximately, 60% of the total N is considered available in slurries and in liquid fractions (MADRP, 2018)

Table 3 allows the discussion of the results from a "user-friendly" point of view, and the real possibility of replacing totally, or partially, the mineral fertilizers with manure-based fertilizers. The information on the N_{av} :P₂O₅ ratios allows, for instance, the selection of materials richer in available N, and poor in P, to avoid the usual surplus of P when applying animal manure to the soil (Sommer et al., 2015). This condition is fulfilled by the LIQ fractions, but with the disadvantage of increasing the quantity of material needed to provide the necessary amount of nutrients (e.g., see the amounts needed to provide 100 kg N ha⁻¹, Table 3), or with the application of the A-SOL fractions, more concentrated, while reducing the amount of material needed to provide the same quantity of N to the crops. In the case of raw PSM, or their LIQ

Table 3

Quantity of manure or slurry (raw or treated) needed to provide 100 kg N ha⁻¹ and estimated available N content (N_{av} ; according to MADRP, 2018) N_{av} : P₂O₅: K₂O ratio, amount of macronutrients and amount of organic C provided by the application of that quantity of manure.

Specie	Treatment	Total N	t ha ⁻¹	Nav	Nav:P2O5:K2O	Total P2O5	Total K ₂ O	Total Mg	Total Ca	Total S	TOC
		kg ha ⁻¹		g kg-1	ratio	kg ha⁻¹	kg ha⁻¹	kg ha ⁻¹	kg ha ⁻¹	kg ha ⁻¹	kg ha ⁻¹
$BOV+^*$	SLU	100	53.76	1.86	1.00-1.41-0.37	70.97	267.74	33.33	58.06	0.54	1303.23
	LIQ	100	61.73	1.62	1.00-3.77-0.90	26.54	111.73	22.84	39.51	12.96	771.60
	SOL	100	35.46	2.82	1.00-2.76-1.58	36.17	63.48	57.45	91.84	21.63	1945.04
	A-SLU	100	52.91	1.89	1.00-1.28-1.00	78.31	100.00	37.04	68.78	219.05	1333.86
	A-LIQ	100	57.67	1.73	1.00-1.19-0.92	84.20	109.00	40.37	59.98	229.53	722.61
	A-SOL	100	40.06	2.50	1.00-1.84-1.69	54.49	59.29	22.84	49.68	147.04	1981.57
BOV-	SLU	100	47.21	2.12	1.00-1.31-0.66	76.49	151.56	26.44	93.01	64.68	1892.82
	LIQ	100	71.84	1.39	1.00-2.63-1.53	38.07	65.37	17.96	40.95	12.21	638.65
	SOL	100	35.24	2.84	1.00-0.91-3.30	109.94	30.30	28.89	68.01	23.26	1996.83
	A-SLU	100	48.31	2.07	1.00-1.12-2.38	89.37	42.03	24.64	59.90	189.86	1827.54
	A-LIQ	100	61.73	1.62	1.00-0.95-1.71	105.56	58.64	32.72	59.88	216.05	771.60
	A-SOL	100	34.79	2.87	1.00-1.21-2.99	82.46	33.40	22.62	66.81	172.23	2670.84
PSM	SLU	100	127.23	0.79	1.00-1.16-1.33	86.51	75.06	34.35	68.70	0.00	1276.08
	LIQ	100	208.33	0.48	1.00-1.85-1.85	54.17	54.17	20.83	20.83	6.25	310.42
	SOL	100	26.25	3.81	1.00-2.35-8.28	42.52	12.07	45.67	109.71	21.00	1810.50
	A-SLU	100	152.91	0.65	1.00-0.83-2.52	120.80	39.76	38.23	82.57	142.20	1140.67
	A-LIQ	100	208.33	0.48	1.00-0.68-1.66	147.92	60.42	43.75	93.75	193.75	545.83
	A-SOL	100	36.95	2.71	1.00-1.36-8.20	73.54	12.20	38.80	63.93	60.24	2364.38
PSF	SLU	100	27.06	3.70	1.00-0.99-0.78	101.19	127.44	34.36	70.62	25.97	1494.05
	LIQ	100	30.25	3.31	1.00-4.24-1.88	23.59	53.24	7.86	35.69	14.82	544.77
	SOL	100	16.89	5.92	1.00-0.54-2.83	186.25	35.29	58.09	98.95	24.32	1817.46
	A-SLU	100	25.33	3.95	1.00-0.97-1.94	103.34	51.42	49.90	70.92	139.06	1239.87
	A-LIQ	100	27.46	3.64	1.00-0.88-1.73	114.22	57.66	37.34	50.52	127.92	564.80
	A-SOL	100	21.45	4.66	1.00-1.20-2.59	83.23	38.61	27.24	87.52	131.92	2105.32
CAT		100	63.69	1.57	1.00-0.44-0.84	225.48	119.75	87.90	128.66	0.64	5441.40
GOA		100	39.53	2.53	1.00-0.95-3.09	105.14	32.41	79.45	309.88	0.40	4433.99
POUL		100	9.34	10.71	1.00-0.91-0.54	109.39	184.12	44.84	110.14	0.93	3197.76

Bov+: Intensive Cattle Slurry; Bov-: Cattle Slurry; PSM: Pig Slurry with all stages of pig production; PSF: Pig Slurry from fattening farm; CAT: Cattle Manure; Goa: Goat Manure; POUL: Poultry Manure. SLU: Non-treated Slurry; LIQ: Liquid Fraction; SOL: Solid Fraction; A-SLU: acidified Slurry; A-LIQ: Liquid Fraction of the acidified Slurry; A-SOL: Solid Fraction of the acidified Slurry; N_{av}: estimated available nitrogen.

fractions, for instance, the amounts needed to supply 100 kg N ha⁻¹ would be enormous (127.23–208.33 t ha⁻¹), hindering the use of this material as an integral substitute for mineral fertilization, or to the exportation of their nutrients content, leaving that hypothesis only to its solid fractions (SOL or A-SOL). On the opposite side, for instance, POUL only requires a small amount of material to provide a large amount of N (e.g., about 9.3 t to provide 100 kg N ha⁻¹, Table 3), with the bonus of providing other nutrients, except P, which may be, eventually, supplied by the use of other manure derived materials, richer in P (e.g., the solid fraction of PSF), or supplemented with a mineral fertilizer.

One aspect that it is important to highlight, and that is obvious from Table 3, is that these materials can suppress the needs of the crop, partially or totally, not only regarding N, P and K, but also for the secondary macronutrients (Mg, Ca and S, Table 3). Another positive point, relative to the use of mineral fertilizers, is the addition of organic C to the soil. In fact, taking, for example, POUL, the referred application dose (9.3 t ha⁻¹ year⁻¹ to provide 100 kg N), will correspond to an input of 3197.8 kg ha⁻¹ year⁻¹ of exogenous C, which can be an important contribution to the increase of the soil organic carbon pool.

An adequate supply of nutrients, combined with organic matter, is crucial to ensure a high quality production in agriculture (Souri et al., 2018) and it can be beneficial towards soils health. The uncertainty of nutrients availability on a manure-based fertilizer may lead to unbalanced inputs of other elements, like P (Keskinen et al., 2020). These authors did accomplish the refining of broiler manure as a N fertilizer, allowing to adjustment of the amount of amendment required to a specific purpose, promoting the agronomic enhancement of this nutrient resource. Also, Mažeika et al. (2021) assessed the agrochemical efficiency of the granulated organic and organo-mineral fertilizers obtained from chicken manure waste, demonstrating that its application can keep a constant nutrient concentration in soil with a double benefit of minimizing the mineral fertilizer environmental impacts. It can be then stated that it is possible to produce manure-based fertilizers by concentrating nutrients and altering the N:P ratio to a more adequate

and known value, one of the specifications most valued by farmers (Tur-Cardona et al., 2018), but it require the blending of manures or sub products of the treatments applied. However, more studies will be essential to understand the nutrients dynamics in soil and ensure that both scenarios proposed (farm scale or centralized level) close the nutrients loops and offers a sustainable hypothesis towards a circular economy.

4. Conclusion

In this study, it was possible to identify the most promising materials for the production of tailor-made organic fertilizers as well as those that do not fulfil the needed requirements, due to feasibility issues, e.g., the large quantity of PSM or its liquid fractions (LIQ, A-SLU and A-LIQ) required to supress the crops needs. Indeed, some of these materials can individually solve some of the problems initially pointed out, namely the unbalanced nutrients ratio of manures relatively to plant requirements that usually lead to the overapplication of P. Nevertheless, these lowtechnological demanding techniques may not be sufficient to produce the intended manure-based fertilizer with a known N:P ratio but will surely help to cope with the reality towards a more sustainable agricultural practice. The results obtained in this study demonstrated that the blending of some of these materials has a strong potential to the production of specific manure-based fertilizer.

More studies are needed to properly assess some potential interesting blends and some questions still need to be solved, namely the behaviour of the materials when blended to produce a possible manure-based fertilizer in both scnearios considered, which may differ from their individual performance.

CRediT authorship contribution statement

Joana Prado: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Validation, Roles, Writing – original draft, Writing – review & editing. **Henrique Ribeiro:** Conceptualization, Formal analysis, Methodology, Supervision, Validation, Writing – review & editing. **Paula Alvarenga:** Conceptualization, Data curation, Methodology, Supervision, Validation, Writing – review & editing. **David Fangueiro:** Conceptualization, Formal analysis, Funding acquisition, Investigation, Methodology, Project administration, Resources, Supervision, Validation, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.The study was supported by the Project Nutri2Cycle: H2020-SFS-30-2017- "Transition towards a more carbon and nutrient efficient agriculture in Europe", funded from 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).

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Appendix A. Supplementary data

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