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Abstract

Pig (*Sus scrofa domestica*) slurries (PS) are widely applied to soil as fertilisers. Compositional variability, as shown in this study, is the main constraint on their efficient use. Slurry samples, collected from 126 commercial pig farms were analysed and organic nitrogen (ON), ammoniacal nitrogen (AN), total nitrogen (TN), total potassium (TK), total phosphorus (TP) content, pH, EC (electrical conductivity), DM (dry matter) and OM (organic matter) quantified. Relationships between major nutrient contents of PS and its physical and chemical properties were analyzed. Ammoniacal-N and TK were linearly related to EC ($p<0.0001$) for values lower than 5.6 kg [AN] m^{-3} and 5 kg [TK] m^{-3} with coefficients of determination (R^2) of 0.86 and 0.58 respectively, in agreement with previous linear models. At higher AN values (which means EC > 40 dS m^{-1}) linearity cannot be maintained, which has important consequences for direct slurry EC measurements. Organic N and TP in slurries were closely related ($p<0.0001$) to DM with R^2 of 0.90 and 0.68 respectively.

Keywords: compositional-variability; fertilizer-value; nutrients, physicochemical models; pig slurry.

Nomenclature

Abbreviations:

AN	Ammoniacal nitrogen
ANOVA	Analysis of variance
d	Index of agreement
DM	Dry matter
DMRT	Duncan’s multiple range test
EC	Electrical conductivity
ICP AES	Inductively coupled plasma atomic emission spectrometry
IS	Ionic strength
MAE	Mean absolute error
MEF	Modeling efficiency statistic
NIRS	Near infrared reflectance spectroscopy
NS	Non-significant
OM	Organic matter
ON	Organic nitrogen
PS	Pig slurry
RMSE	Root mean square error
SD	Standard deviation
TK	Total potassium
TN	Total nitrogen
TP	Total phosphorus

Symbols:

n	Number of observed values

$\hat{O}$	*A*verage of the observed values
O_i	Observed values for the *i*th data
P_i	Predicted values for the *i*th data
r	Pearson correlation
R^2	Coefficient of determination

1. Introduction

Livestock produce large amounts of manures which contain a wide range of plant nutrients as nitrogen (N), phosphorus (P), potassium (K) or micronutrients, which are recycled in agricultural systems for the production of food and fibre for humans and feeds for livestock. If they are used properly, they can replace significant amounts of chemical fertilisers. Crop nutrient requirements and available soil nutrient concentrations determine the amount of nutrients to be applied.

Pig production in Spain was 26 million head in 2009 which represents 17% of total European Union (FAO, 2011). The autonomous regions of Aragon and Catalonia contain around 42% of Spanish pig production. In Spain, it is a common practice to apply slurries as fertiliser in agricultural systems and N, P, and K in slurries should be quantified in order to avoid nutrient losses and to achieve maximum efficiency in crop nutrition. Furthermore, during recent years, laws and directives in Europe have been enforced, in order to reduce environmental impacts, by limiting N application to 170 kg N ha^{-1}, according to the Nitrate Directive (European Union, 1991). Pig slurry is characterised by its low dry matter content and the predominance of the ammoniacal-N (AN) in total N (TN) content. Once added to the soil, slurry AN quickly transforms into nitric-N, and it may be fully assimilated by crops if not leached. Also, its K and P content are available to crops in a similar way to those from mineral fertilisers (Irañeta et al., 1999; Eghball et al., 2005). As reported in the literature, the composition of pig slurries vary to a great extent due to factors such as farm management, animal diet, water management and storage duration. For instance, slurry composition can be related to the length of the storage period in the pit (Ndegwa et al., 2002; Ndegwa & Zhu, 2003; Balsari et al., 2006; Yagüe et al., 2011). Manure application rates are generally designed to meet crop growth requirements for N. However, the ratio of N to P, using an N-based system, can supply the soil with much more P than the crop requires, a consideration which is of environmental concern (Sharpley et al., 2006).

To allow the efficient use of slurry as a fertiliser, characterisation of its nutrient content (N, P and K) before application must be implemented. Traditional analyses in laboratories provide great precision, but their cost and the time needed to obtain results have not been attractive to many farmers. Therefore, farm-level methods to estimate the nutrient concentration of livestock manure are required. Rapid and low cost estimation methods can be divided into two types: indirect methods (i.e. physicochemical models) and direct methods (i.e. rapid methods of nutrient measurement).

Physicochemical models relate slurry nutrient content with physicochemical properties such as specific gravity, dry matter content (DM), pH or electrical conductivity (EC), as reported by many researchers (Tunney, 1979; Scotford et al., 1998; Zhu et al., 2003; Moral et al., 2005; Yang et al., 2006b; Martínez-Suller et al., 2008; Suresh et al., 2009; Chen et al., 2009a). Near-infrared reflectance spectroscopy (NIRS) has been also used for quantifying nutrient content in animal manures: from pigs (Malley et al., 2002; Yang et al., 2006a), dairy cows (Reeves & Van Kessel, 2000; Van Kessel and Reeves, 2000) or poultry (Reeves, 2001; Xing et al., 2008) but implementation for farmers, compared with other available methods (i.e. densitometry or conductivity measurement) is expensive and its use is quite tedious at a field level. Determination of specific gravity, DM, pH or EC can help to quantify available nutrient content (N, P and K) in slurries, in order to establish their fertiliser value and promote their use in agriculture, thus saving mineral fertilisers at the farm level and reducing undesired negative environmental side-effects.

The objectives of our research were: (i) to evaluate nutrient variability in pig slurries by determining N, P and K according to farm type in the northeast of Spain; (ii) to generate physicochemical models for predicting pig slurry nutrient content using information from a wide range of samples from different type of farms; (iii) to validate physicochemical models obtained from references from the literature using our slurry samples in order to predict their usefulness and constraints in TN, AN, TK and TP determinations.

2. Materials and methods

2.1. Slurry source

Slurry samples were collected from 126 different pig farms in Aragon and Catalonia (NE Spain). The pits were in static conditions. Slurry samples were directly obtained from pits and each one was stored in a closed bottle immediately after their aspiration. Approximately 2-3 l of PS were sampled, kept as cool as possible upon arrival at the laboratory and stored at low temperature (3-5ºC). Samples were classified in three types: from fattening farms (*n*=57; pigs from 12-16 kg up to 90-110 kg); from maternity farms (*n*=36; including pregnant sows, lactating sows and piglets up to 12-16 kg) and closed cycle farms (*n*=17) which include sows and fattening production systems (with slurries being stored in the same pit).

2.2. Sample analysis

The parameters and the analytical methods done in the laboratory were: AN by the modified Kjeldhal method (Devarda without digestion), gravimetric DM content at 105ºC, pH by potentiometry (1:5 dilution), EC at 25ºC by conductivity measurement, organic matter (OM) by calcination at 550ºC and organic nitrogen (ON) by the Kjeldahl method using conventional laboratory analysis (APHA, 1998). Total phosphorous (TP) and total potassium (TK) were analysed by acid digestion (wet) and further determined with inductively coupled plasma-atomic emission spectrometry (ICP AES, USEPA, 1992).

2.3. Physicochemical models

Several physicochemical models of PS nutrient content have been developed and are available in the research literature (Table 1). They were selected for validation according the information on the range of nutrients used for the tests and their date of publication.

2.4. Statistical Analysis

The following criteria were used to assess the performance of the different physicochemical models found in the literature review (Table 1): intercept (*a*) and slope (*b*) values of linear regression between simulated and observed data for each model; the root mean square error (*RSME*; Eq. 1); the modeling efficiency statistic (*MEF*; Eq.2; Tedeschi, 2006); mean absolute error (*MAE*; Eq. 3) and the *d*-index of agreement (Eq. 4; Wilmott, 1982) that is an aggregate overall indicator that is a better criterion than R^2. *RMSE*, *MEF*, and *d* were computed as follows:

$$\mathrm{RMSE} = \left[\frac{\sum_{i=1}^{n} (P_i - O_i)}{n} \right]^{-0.5} \qquad \text{[Eq. 1]}$$

$$\mathrm{MEF} = 1 - \left[\frac{\sum_{i=1}^{n} (Pi - Oi)^2}{\sum_{i=1}^{n} (Oi')^2} \right] \qquad \text{[Eq. 2]}$$

$$\mathrm{MAE}=\left[\frac{\sum_{i=1}^{n}\left|P_i-O_i\right|}{n}\right] \quad \text{[Eq. 3]}$$

$$d=1-\left[\frac{\sum_{i=1}^{n}(P_i-O_i)^2}{\sum_{i=1}^{n}\left(\left|P_i'\right|+\left|O_i'\right|\right)^2}\right] \quad \text{[Eq. 4]}$$

Where n is the number of observed values, O_i and P_i are observed and predicted values for the ith data pair, $P_i{'}=Pi\text{-}\hat{O}$ ($\hat{O}$: average of the observed) and $O_i{'}=Oi\text{-}\hat{O}$.

According to Willmott (1982), the model fit improves as index approaches unity and *RMSE* approaches zero. In a perfect fit, *MEF* would result in a value equal to one. If *MEF* is lower than zero, the model-predicted values are worse than the observed mean. The *MEF* statistic may be used as a good indicator of goodness of fit (Mayer and Butler, 1993).

In the statistical analysis, analysis of variance (ANOVA), correlations and regressions, significance levels were indicated using the following probability (p) levels: * $0.05 \leq p < 0.01$; ** $0.01 \leq p < 0.001$, *** $0.001 \leq p < 0.0001$. Values of p, higher than 0.05, are considered non-significant (NS). Duncan's Multiple Range Test (DMRT) was computed for comparing all possible pairs of means. If the regression between variables is significant and the size of the coefficient of determination (R^2) is ≥ 0.70, we consider that fits are acceptable. The statistical analysis was performed using the statistical package SAS V8 (SAS Institute, 1999-2001).

3. Results and discussion

3.1. Physicochemical composition: variability in nutrient fertiliser value

The main component of PS is water. In this study (*n*=126) average DM content was 63.6 kg m^{-3} (Table 2) which means an average water content close to 94%. The low nutrient to volume ratio implies that large volumes of slurry need to be transported, this being the limiting factor on the distance that slurry can be economically used as fertiliser. This distance can be roughly doubled if slurry from a fattening farm is used compared with a sow farm, due to its much higher nutrient content (Yagüe et al., 2006). The trend is to reduce slurry volume production in a farm, which is a powerful tool in waste-nutrient management planning (Teira-Esmatges & Flotats, 2003) because it increases nutrient concentration in PS and reduces transportation costs.

The statistics for all datasets and for each type of farm are given in Table 2. Most of the slurries analysed had a neutral-basic pH up to a maximum value of 9.1. Only 8 samples of the total 126 analysed in the present study had a pH lower than 7.

Electrical conductivity (EC) varied over a range from 8.7 to 45.0 dS m^{-1} and the mean value was 26.8 dS m^{-1} (Table 2). This range is somewhat higher than that of the data obtained by Moral et al. (2005) and Martínez-Suller et al. (2008) where it ranged from 12.8 to 25.2 dS m^{-1} and 3.6 to 38.1 dS m^{-1}, respectively. Also, it is lower than data from Sánchez & González (2005) and Suresh et al. (2009) where it ranged from 2.0 to 75.2 dS m^{-1} and 0.5 to 58.0 dS m^{-1} respectively, probably linked to the dietary intake of salts.

The variability for DM and OM content was high, from 6.9 to 238.2 kg m^{-3} and from 4.3 to 182.2 kg m^{-3} respectively. This variability, according to Leiros et al. (1983), can be explained by the rainfall received during storage in open pits while, in closed pits, the most important dilution factor is the different amount of cleaning water used in farms. In addition, stratification in the pits when no mixing takes place, increases variability in parameters associated with the solid slurry fraction (Ndegwa et al., 2002; Ndegwa & Zhu, 2003; Yagüe et al., 2011).

The nutrients NPK varied over a wide range; 1.3 to 10.1 kg [TN] m^{-3}, 0.9 to 7.5 kg [AN] m^{-3}, 0.3 to 6.0 kg [ON] m^{-3}, 0.2 to 8.1 kg [TP] m^{-3} and 0.8 to 20.1 kg [TK] m^{-3}. As far as the TP dataset is concerned, 79% of samples had < 2 kg [TP] m^{-3}; also, 55% of values fell into the range 0.09 - 0.99 kg [TP] m^{-3} and 45% into 1.00 - 1.99 kg [TP] m^{-3}. Similar ranges were found by Chen et al., (2009a) in their recompilation dataset of different experiments, where more than 70% of samples had a TP content < 2 kg [TP] m^{-3}. In relation to ON dataset, 64% of samples had less than 2 kg [ON] m^{-3}, with 45% of values in the range of 0.09 - 0.99 kg [ON] m^{-3} and 55% in the range 1.00 - 1.99 kg ON m^{-3}. This can be explained since the greater part of the samples were taken from lagoon slurry and only a few from the sediment, in the deeper layer of the pit, where TP concentration increases in association with total solids accumulation (Ndegwa et al., 2002), and a similar trend occurs for ON. The rest of the nutrients (TN, AN, and TK) show a more uniform average distribution along the obtained range of values (Fig. 1a) although they are influenced by the number of samples taken for each group and by the nutrient content according to farm type which differs (Table 3).

Ammoniacal-N represents, on average, 69%, 72% and 62% of TN for fattening, maternity and closed cycle farms, respectively. The range of the AN/TN ratio was 0.36-0.89 (Table 2) which includes the 0.60-0.70 ratio mentioned by Bertrand (1993), the 0.66-0.73 ratio found by Ferrer et al. (2000) and also the 0.70 ratio described by Christensen et al. (2009) in PS. Ammoniacal-N content is closely related to animal physiological state and feeding; as adults have a higher catabolism than growing pigs the proportion of ureic N is higher (Sánchez & González, 2005). Nevertheless, lowest ratio values indicate that important Ammoniacal-N losses can exist in open pits of Mediterranean farms with high slurry pH which favours ammonium losses as ammonia (Balsari et al. 2006; Yagüe et al., 2011).

The average ratio of major nutrients N:P:K (1:0.3:0.8), remains almost constant in the total dataset and in the data from the three different farm types (Table 3), No correlations between TN, AN, TP, and TK contents were observed. Similar mean values of N:P:K ratios were reported by Levasseur (2002) for pig fattening farms (1:0.3:0.9). However, the values reported here were somewhat different from the values reported by Sánchez & González (2005) which were 1:0.3:0.4 (N:P:K). Although the agreements in N:P ratios, in this last reported papers, with our data, an important dispersion exists. In our data (Table 2), TP content ranged from 0.1 up to 1.5 times higher and coefficients of variance were 71%, 67%, 108% for fattening, maternity and closed cycles respectively, while TK content ranged between 0.2 up to 4.0 times higher than TN content. This means than N:P:K ratio must be established for each slurry sample and a general value provided by previous authors (Levasseur, 2002; Sánchez & Gonzalez, 2005) is regarded as not being useful.

According to data presented in Table 2, farm type has an influence in the main physicochemical parameters of PS, except for TP. This can be explained because the samples come from farms where slurries are not mixed in the pits before being spread over land. Total P concentration changes with pit depth, associated with stratification or sedimentation of solids, as it is mainly found in the solid fraction (Duthion et al., 1979) also, according to Sánchez & González (2005), around 90% of TP is excreted in the faeces in the solid fraction, the rest is dissolved mainly in inorganic form. Thus, in static pits, part of P in the liquid phase is dissolved in urine and other part is suspended, linked to small solid particles (some particle size stratification in the pit profiles exists), which explains that 78% of PS samples had a TP concentration lower than 2 kg P m^{-3}. Ndegwa et al. (2002) found that TP concentrations in liquid slurry fractions were between 0.5 and 2.0 kg [TP] m^{-3} and concentrations increased up to 3-5 kg m^{-3} P values in the bottom or in the top (crust formation) of pits, associated with an important accumulation of total solids. Higgins et al. (2004) evaluated TP concentrations as a function of PS loads pumped from different depths in the pit and showed relatively constant numbers in the liquid fraction but dramatic changes in TP from the last loads removed at the deeper pit layers, which illustrates the positive correlation between total solids and TP. This research indicates the need to quantify TP data content for individual loads, to avoid excess of soil P content when applying over land. The TP concentration behaviour in static pits may need to condition phosphorus fertilisation strategies in the long term for each field receiving slurries.

When other nutrients are compared between types of farms, fattening slurries have around 53% AN, 71% TK and 46% TN higher nutrient content than other farm types.

In fattening farms (Table 3), the average DM content of slurries (74.0 kg m^{-3}) was 56% and 31% higher than values from maternity or closed cycle respectively. Also, average EC (30.6 dS m^{-1}) is 42% and 34% higher than values from maternity and closed cycle, respectively. Nevertheless, average nutrient values from different types of farms can be double the values obtained from other areas of Spain (Moral et al., 2005) which also indicates differences in animal diets and in farm water management.

3.2. Correlations to estimate nutrients in pig slurries and regression equations

Correlations between nutrient content of slurries and easily analysed parameters (EC and DM) were highly significant ($p<0.001$, Table 4).

Electrical conductivity was well correlated to ionic species in slurries; AN (0.90) and TK (0.78). It can be also correlated to TN (0.79) probably because Pearson correlation value (r) was 0.88 between AN and TN. Dry matter was well correlated to OM ($r = 0.99$), ON ($r = 0.95$) and TN ($r = 0.78$). Both parameters, DM and EC, are frequently used to estimate the fertiliser value of manures (Stevens et al., 1995, Zhu et al., 2003; Moral et al., 2005; Martínez-Suller et al., 2008). On the other hand, Higgins et al. (2004) suggest that TN may be more dependent on the animal growth stage/storage facility than total solids content, which agrees with the AN/TN ranges found (Table 2). However, PS undergoes changes during pit storage that could change the relationship between nitrogen forms because of the ON association with the solid fraction (i.e. changes due to sedimentation process) and the AN association with liquid fraction (i.e. changes due to ammonia volatilisation).

Phosphorus, as an organic-dependent parameter which is also associated to the solid fraction, was correlated (Table 4) to DM ($r = 0.78$), OM ($r = 0.76$) and ON ($r = 0.74$). The average TP/ON ratio was 0.90 ± 0.5 (± SD) for all datasets, but although both nutrients are linked to the solid fraction of slurry they did not show a constant ratio (Table 2).

Pearson coefficient between AN and TK free ions was 0.51 probably because their ratio can also change during pit storage (Table 4). Ammoniacal-N can be lost from open storage facilities to the atmosphere at different rates under the influence of different environmental factors, such as temperature, wind speed or solar radiation (Portejoie et al., 2003). Potassium concentration in slurry is a constant or can increase if time-lag in pit is long enough to have significant water evaporation losses. As water evaporates, volume reduces and salt concentration increases (Yagüe et al., 2011). This fact (ammonia volatilisation losses and potassium concentration increment in the slurry) shows an AN/TK ratio with an important variability (Table 2), average value including all data was 0.96 ± 0.4 (± SD). The semiarid Mediterranean climate in the area provides favourable conditions for ammonia volatilisation from pits and also favours increments in TK concentration of the stored slurries.

Linear regressions were derived, including all data sets, and acceptable fits were obtained between the analysed physicochemical parameters (EC and DM) and the main nutrients in PS (Fig. 2 and 3). Nevertheless, although the observed AN and TK correlation with EC<40 dS m^{-1} has a consistent linear relationship beyond the 40 dS m^{-1} linear relationship cannot be maintained. Previous studies (Moral et al., 2005; Provolo & Martínez-Suller, 2007; Martínez-Suller et al., 2008) had EC values lower than 40 dS m^{-1}; only Sánchez & González (2005) had values up to 40 dS m^{-1} but they did not focus on nutrient-EC relationships. Suresh et al. (2009) measured EC up to 58 dS m^{-1} and the best fit for AN and TN versus EC was an exponential equation (R^2 = 0.91 and 0.74 respectively, Table 1) and for TK versus EC, best fit was a quadratic equation (R^2 = 0.69, Table 1).

Electrical conductivity in slurries is governed by the concentrations of the major cations dissolved in the liquid phase (Na^+, K^+, Ca^{+2}, Mg^{+2}, NH_4^+) balanced by anions with the same total negative charge. As most monovalent salts are almost completely dissociated in water, and K^+ and NH_4^+ are the dominant cations in slurries, they can be correlated to EC (Stevens et al., 1995). The EC is a measure of effective ionic strength (IS) but according to Sposito (2008) and experiments with soil solutions, the Marion and Babcock (1976) equation: log IS=1.159+1.009 log EC is only accurate for IS up to 300 mol m^{-3}, which means for EC up to 37.86 dS m^{-1} because the ion-pairing effect alters the linear relationship. The principal factors that influence EC in aqueous solutions are the nature and concentration of solutes, the degree to which the solutes are dissociated into ions, the charge on each ion, the mobility of each ion, and temperature of the solution (Hem, 1982). This boundary agrees with the EC limit value found in this study for linear relationships; AN vs. EC and TK vs. EC. An increasing IS of the liquid will affect flocculation processes due to a reduced electrostatic repulsion (Hjorth et al., 2010). We detected this fact for EC values > 40 dS m^{-1} which adjust to AN values > 5.6 kg m^{-3} and TK values > 5 kg m^{-3}.

Dry matter (Fig. 3) was the best significant parameter ($p<0.001$) for fitting ON (R^2 = 0.90) and TP (R^2 = 0.68) which can be explained as they are related to the slurry solid fraction (Ndegwa et al., 2002; Yagüe et al., 2011) and also because of the strong correlation (r = 0.99) between DM and OM. However, for TP a more significant relationship can be found for samples with DM< 125 kg m^{-3}, which includes 79% of the dataset, and also relates to maximum TP concentration in pit storage solution under static conditions (< 2 kg m^{-3}). This new relationship has the same R^2 value.

Thus, in the case of slurries with low DM content, such as pig slurry, separation into 2 fractions > 2000 μm and < 2000 μm would allow the removal of most of the solids and phosphorus from the liquid phase (Fangueiro et al., 2010), which has important agronomic implications (i.e. requiring fertilisation adjustments) when the different fractions are applied in the field. This could be also the case when flocculating additives for slurry are used (Hjorth et al., 2010), because additives flocculates the solid fraction which mainly contains the TP amount and, as the solid fraction separates from the liquid fraction, two different products for fertiliser use are obtained.

If DM vs. TP models are compared with those which have R^2 values higher than 0.68, their TP values are lower than 2 kg [TP] m^{-3} (Scotford et al., 1998; Moral et al., 2005), which suggests that they were calculated from samples associated with the slurry liquid fraction or from diluted slurries. The models with higher TP content (4 or 9.1 kg [TP] m^{-3}) had lower R^2 values, between 0.37 to 0.43 (Martínez-Suller et al., 2008 and Zhu et al., 2003). Our model includes a wide range of TP contents (up to 6.0 kg m^{-3}; $R^2 = 0.68$), which allows it to be used in pits under static conditions, where sedimentation takes place.

3.3. Evaluation of physicochemical models: model comparisons

Our measured data was compared with nutrient contents predictions by various physicochemical models (Table 1) as shown in Fig. 4. The TN physicochemical models (Fig. 4a) were significant ($p<0.0001$) with an $R^2= 0.63$, and *d* index between 0.69 and 0.89 (Table 5) but the model proposed by Suresh et al. (2009) gave the best predictions (RMSE= 1.37; MAE= 0.95; MEF= 0.59; d= 0.89), probably because it was the only one that included, in its development, EC values higher than 40 dS m^{-1}.

For AN content Suresh et al. (2009) also gave the best fit (RMSE= 0.64; MAE= 0.46; MEF= 0.78; d= 0.95). Two models (Moral et al., 2005; Martínez-Suller et al., 2008; Fig. 4b) had good fit up to 5.6 kg [NH_4-N] m^{-3} content (which is also the maximum value used) but above this value only Suresh et al. (2009) gave good results. It was observed that at higher EC (> 40 dS m^{-1}) the behaviour was not linear, as also observed by Suresh et al. (2009). When considering all our data (values higher than 5.6 kg [NH_4-N] m^{-3} are included) a linear regression fitted just as well as exponential ($AN= 0.14\ EC-0.32$ and $AN=0.10\ EC^{1.09}$; both with an $R^2 = 0.86$ and significance: $p<0.0001$, Fig. 2a), but for values higher than 5.6 kg [NH_4-N] m^{-3}, when the exponential equation was used, differences between measured and predicted values were reduced (data not shown) when compared to the linear regression equation. The accurate prediction of AN content was acceptable for all three models when AN values < 5.6 kg m^{-3} or CE< 40 dS m^{-1} are included (Fig. 4b).

Figure 4c shows the relationship between measured and predicted TK content by three models. The regression three models had similar indexes: RMSE, MAE, MEF and d-index (Table 5) using all data. However, although the trends in the models were similar they did not fit acceptably. The upper limit content in Moral et al. (2005) and Martínez-Suller et al. (2008) studies was 6 kg [TK] m^{-3} and in both of these references they just present two values inside the 30 - 40 dS m^{-1} range. In Suresh et al. (2009) the upper limit was 7.3 kg [TK] m^{-3} (with only two values between 40 - 58 dS m^{-1}) and a quadratic model was used. Chen et al. (2009a and 2009b) compiled datasets from different authors and countries for cattle and pig slurry and, from their findings, it appears to have an upper limit close to 5 kg [TK] m^{-3} (and EC < 40 dS m^{-1}) using the linear relationships established.

The use of EC as tool to prediction for AN in concentrations > 5.6 kg [AN] m^{-3} indicates an important underestimation of this nutrient by linear physicochemical models. It would be also the case for TK > 5 kg m^{-3} (Fig. 4b and 4c). This fact has important environmental (i.e. N leaching or P accumulation in soil) and agronomic consequences (i.e. excess N, lodging of crops) if they are not taken into account. Furthermore, in the context of a general trend towards the minimisation of PS volume at farm level, in order to reduce transport costs, when this slurry is applied in the field, these concentration boundaries have other practical implications as the number of samples exceeding these limits will increase in Mediterranean areas.

The significant number of cases with high potassium concentration values in PS could be due to an excess in the diet of this nutrient or a relative concentration during storage in open pits. As observed by Scotford et al. (1998) and Martínez-Suller & Provolo (2007), the content of TK and the degree of its correlation with EC varies a lot between geographical locations, and probably because of differences in feeding and management strategies. As an example, soybeans can supply most of the crude proteins needed by pigs, while at the same time soybeans contain high concentrations of K that increase the pH and TK content of urine slurry when excreted (Portejoie et al., 2004).

Physicochemical models for TP based on DM (Zhu et al., 2003; R^2 = 0.46 and Martínez–Suller et al., 2008; R^2 = 0.37, Fig. 4d), when data from our study are used, had a coefficient of determination of 0.61, similar to that obtained when TP was correlated to. DM (R^2 = 0.68; Table 5). The main inconvenience of this estimator is that DM analysis cannot be as easily carried out “in situ” unlike the EC determination.

4. Conclusions

Slurry nutrient content and N:P:K ratios vary between type of farms to a great extent. Pig slurries from fattening farms exhibit higher nutrient content than slurries from maternity and closed cycle farms. Physicochemical linear models are good tools for nitrogen nutrient estimation (the main nutrient where fertilisation restrictions are established) and also they are good for phosphorous estimation but, in both cases, some limitations exist. AN (< 5.6 kg m^{-3}) can be indirectly measured by EC (< 40 dS m^{-1}) and ON and TP can be indirectly quantified from DM. Our model for TP is consistent for a wider range of values (< 6 kg [TP] m^{-3}) than other models found in the literature. Total K shows high variability when it is related to EC (R^2= 0.58) thus, the estimated regression equation would not be sufficiently useful.

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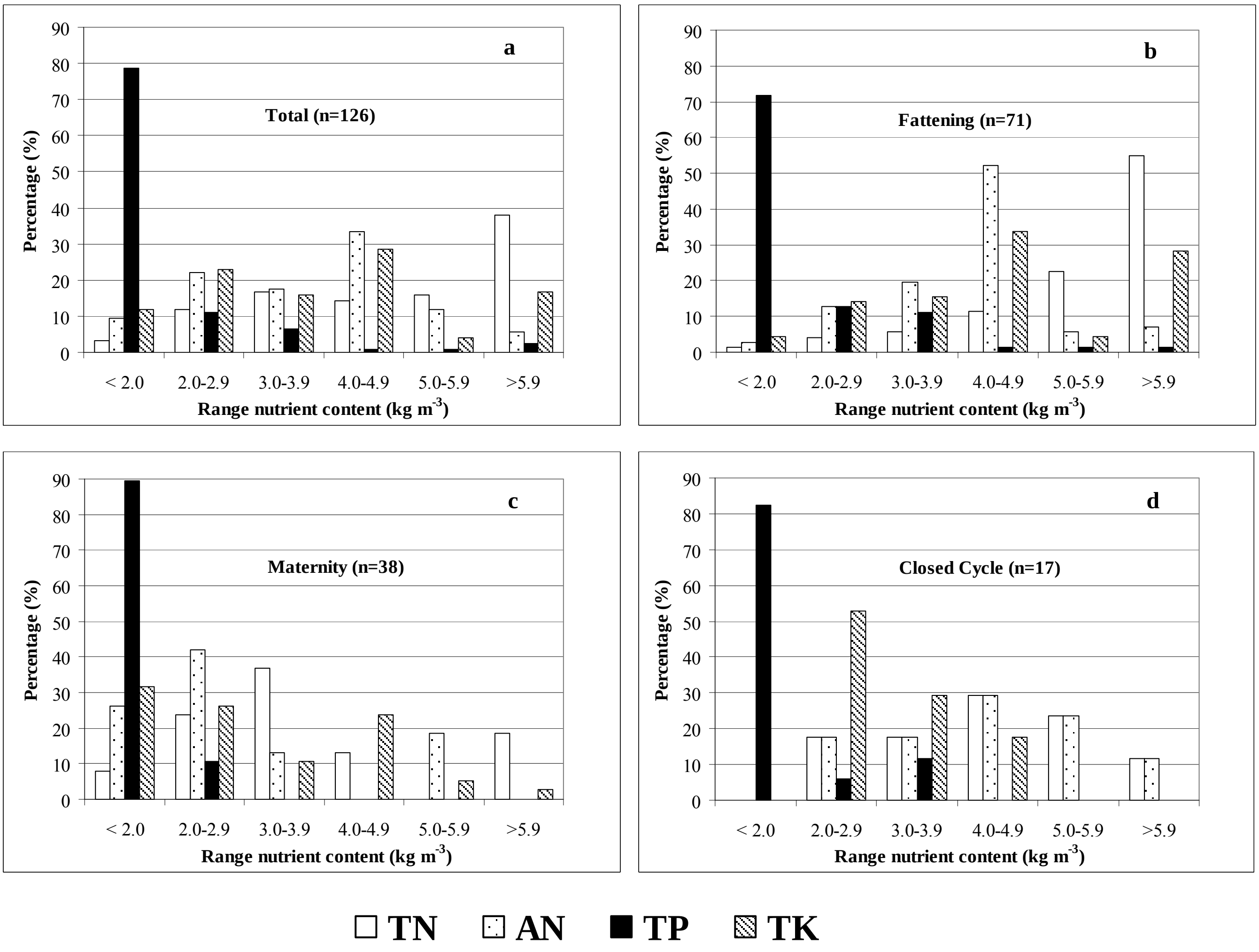
Legend figures

Fig. 1. Sample distribution (a) (%) of total compiled datasets (*n*: number of total analysed samples and for each type of farm) and also according to each type of farm: fattening (b), maternity (c) and closed cycle (d), for total nitrogen (TN), ammoniacal-N (AN), total phosphorus (TP) and total potassium (TK)

Fig. 2. Relationship between (a) ammoniacal-N and (b) potassium versus electrical conductivity for slurry (*** $p < 0.001$)

Fig. 3. Relationship between (a) organic-N, (b) total phosphorus and dry matter (DM) for all different types of farms slurry data (*** $p < 0.0001$)

Fig. 4. Comparison of measured and predicted nutrient content by different physicochemical models: Martínez- Suller et al. 2008 (Mtz); Moral et al. 2005 (Moral); Suresh et al. 2009 (Suresh) and Zhu et al. 2003 (Zhu)



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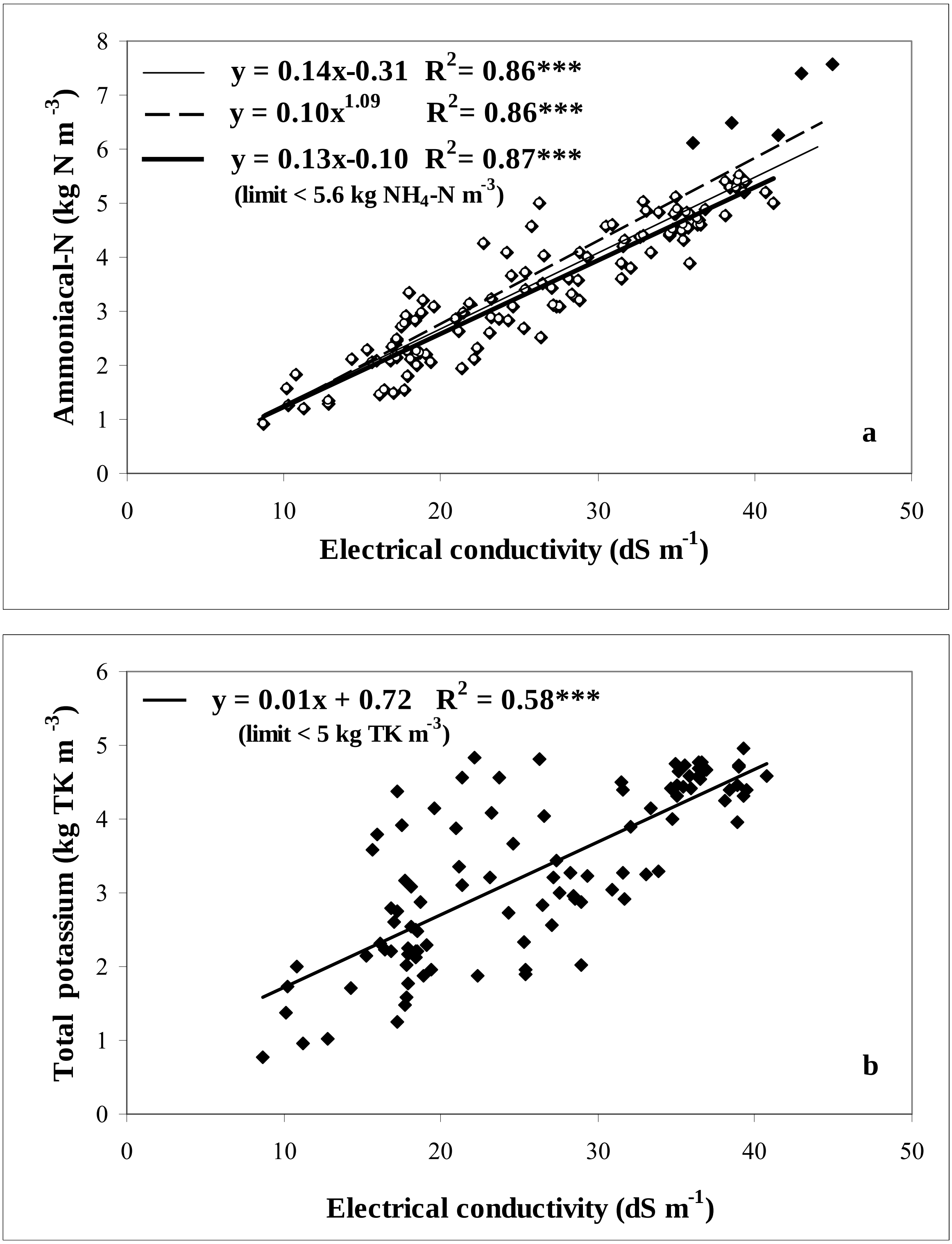

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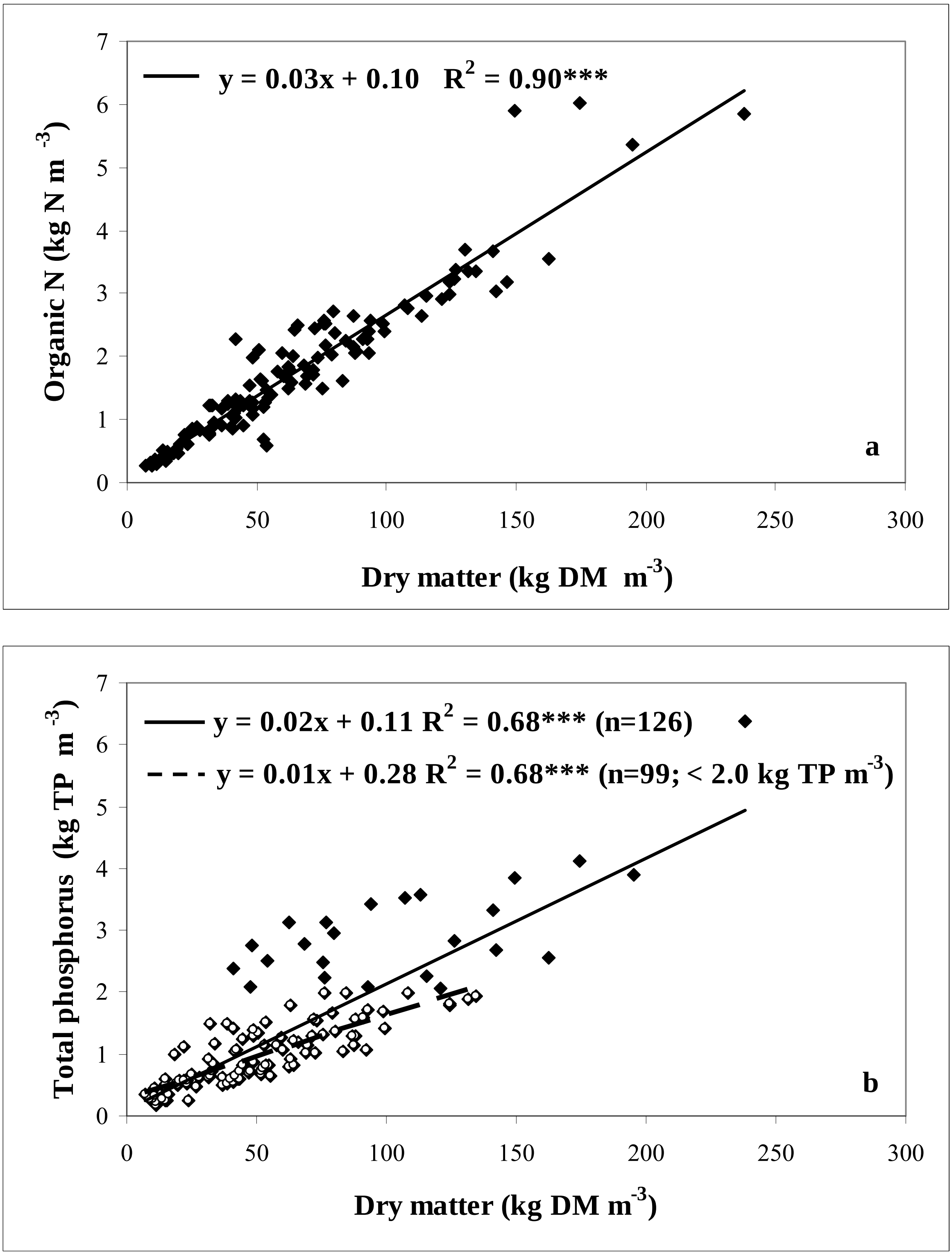

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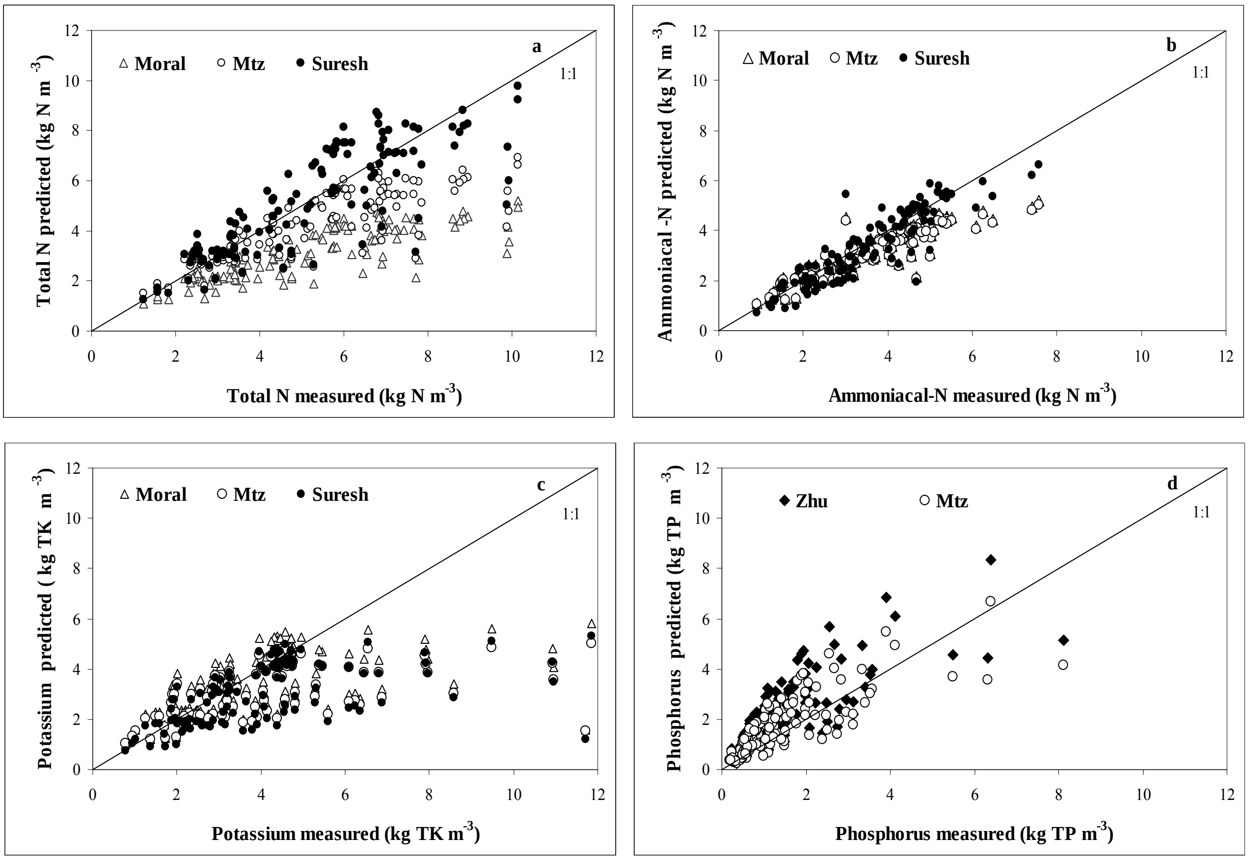

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Table 1. Published physicochemical models for predicting pig slurry nutrient content, regression equations and coefficients of determination (R^2)

Nutrient	**Reference**	**Country**	**Equation**[a]	**Range of nutrient content**	**R^2**
Total Nitrogen (TN)	Moral et al. 2005	Spain	$TN = 0.13EC+0.24$	0.5-5.8	0.78
	Martínez–Suller et al. 2008	Italy	$TN = 0.15EC+0.19$	0.2-5.6	0.78
	Suresh et al. 2009	Korea	$TN = 83.79EC^{1.25}$	0.5-13.0	0.74
Ammoniacal N (AN)	Moral et al. 2005	Spain	$AN=0.11EC+0.10$	0.2-4.5	0.83
	Martínez–Suller et al. 2008	Italy	$AN=0.11EC+0.09$	0.2-5.0	0.82
	Suresh et al. 2009	Korea	AN[b] $= 39.89EC^{1.343}$	0.5-7.5	0.91
Total Potassium (TK) [c]	Moral et al. 2005	Spain	$TK=0.14EC-0.21$	0.2-6.0	0.82
	Martínez–Suller et al. 2008	Italy	$TK=0.11EC+0.04$	0.3-6.0	0.52
	Suresh et al. 2009	Korea	TK[b] $=0.60EC+102.6EC-196.3$	0.5-7.3	0.69
Total Phosphorus (TP) [c]	Zhu et al. 2003	USA	$TP=0.035DM+0.01$	0.1-4.0	0.46
	Martínez–Suller et al. 2008	Italy	$TP=0.03DM+0.05$	0.1-9.1	0.37

[a] Electrical Conductivity (EC) expressed as dS m^{-1}; DM (dry matter), total nitrogen (TN), ammoniacal-nitrogen (AN), total potassium (TK) and total phosphorus (TP) expressed as kg m^{-3}

[b] It was expressed in mg l^{-1}, it was transformed to kg m^{-3} dividing by 1000 the value obtained in equation

[c] Conversion of P to P_2O_5 is done by multiplying by 2.29 and conversion of K to K_2O by multiplying by 1.20

Table 2. Average composition (Mean), standard deviation (SD), maximum (Max.) and minimum (Min.) values of the analysed physicochemical parameters[a] according to type of farm

	Total (n=126)[b]				**Fattening (n=71)**				**Maternity (n=38)**				**Closed Cycle(n=17)**			
	Med.	**Max.**	**Min.**	**SD**	**Med.**	**Max.**	**Min.**	**SD**	**Med.**	**Max.**	**Min.**	**SD**	**Med.**	**Max.**	**Min.**	**SD**
pH (1:5)	8.20	9.10	6.11	0.7	8.39	9.10	7.54	0.4	8.29	9.10	7.56	0.4	7.21	8.70	6.11	1.1
EC (dS m^{-1})	26.84	45.00	8.67	8.5	30.59	45.00	10.28	7.5	21.61	40.70	8.67	9.0	22.84	31.70	15.30	5.7
DM (kg m^{-3})	63.60	238.12	6.89	42.5	73.97	238.12	8.96	44.5	47.37	134.60	6.89	33.8	56.55	146.40	11.48	40.3
OM (kg m^{-3})	42.61	182.16	4.31	31.2	49.61	182.16	5.44	33.7	31.09	95.38	4.31	23.9	39.10	96.03	6.12	28.1
TN (kg m^{-3})	5.30	10.14	1.24	2.1	6.22	10.14	1.58	1.9	3.97	8.85	1.24	2.0	4.48	7.26	2.37	1.4
AN (kg m^{-3})	3.57	7.57	0.91	1.4	4.20	7.57	1.25	1.2	2.81	5.51	0.91	1.3	2.69	4.30	1.46	0.7
ON kg m^{-3})	1.73	6.02	0.26	1.2	2.03	6.02	0.32	1.2	1.16	3.37	0.26	0.8	1.78	3.37	0.29	1.0
TP (kg m^{-3})	1.44	6.38	0.18	1.2	1.68	6.38	0.24	1.2	1.05	2.79	0.22	0.7	1.29	6.31	0.18	1.4
TK (kg m^{-3})	4.38	20.07	0.77	2.9	5.35	20.07	1.73	3.3	3.12	11.71	0.77	2.0	3.16	4.83	2.02	0.8
AN/TN	0.69	0.89	0.36	0.1	0.69	0.89	0.36	0.1	0.72	0.89	0.46	0.1	0.62	0.89	0.40	0.1
AN/TK	0.96	2.02	0.12	0.4	0.94	2.02	0.19	0.4	1.03	1.98	0.12	0.4	0.89	1.47	0.44	0.3
TP/ON	0.90	4.28	0.32	0.5	0.84	4.28	0.32	0.5	1.04	2.82	0.41	0.6	0.75	1.87	0.34	0.4

[a] EC: Electrical Conductivity; DM: Dry matter; OM: Organic matter; TN: Total N; AN: Ammoniacal N; ON: Organic nitrogen; TP: Total phosphorus; TK: Total potassium

[b] n: number of samples analyzed for each type of farm

Table 3. Electrical conductivity (EC), dry matter (DM) and major nutrients content in pig slurry (TN: Total N; AN: Ammoniacal N; ON: Organic nitrogen; TP: Total phosphorus; TK: Total potassium) in the three types of farms (n=126)

	EC	**DM**	**TN**	**AN**	**ON**	**TP**	**TK**	**N/P/K**
	dS m^{-1}	**------------------------------- kg m^{-3}-----------------------------**						
Fattening	30.6A[a]	74.0A	6.2A	4.2A	2.0A	1.7	5.4A	1/0.3/0.9
Maternity	21.6B	47.4B	4.0B	2.8B	1.2B	1.1	3.1B	1/0.3/0.9
Closed cycle	22.8B	56.6AB	4.5B	2.7B	1.8A	1.3	3.2B	1/0.3/0.8
Type farm	***	**	***	***	***	NS	***	-

[a] Within columns, means followed by the same letter are not significantly different according to Tukey multiple range test (0.05)

NS: not significant; ** $0.01 \leq p < 0.001$; $0.001 \leq p < 0 .0001$

Table 4. Correlation matrix between the different slurry properties and nutrients in total pig slurry samples (n=126), numbers are the values of the Pearson correlation (r)

	pH	**EC**[a]	**DM**	**OM**	**TN**	**AN**	**ON**	**TP**	**TK**
pH		0.14	0.02	0.03	0.05	0.15	0.09	0.16	0.26
EC	NS		0.37	0.34	0.79[b]	0.90	0.40	0.08	0.78
DM	NS	NS		0.99	0.78	0.42	0.95	0.78	0.38
OM	NS	NS	***		0.76	0.40	0.94	0.76	0.32
TN	NS	***	***	***		0.88	0.82	0.55	0.56
AN	NS	***	***	***	***		0.44	0.24	0.51
ON	NS	***	***	***	***	***		0.74	0.44
TP	NS	NS	***	***	***	**	***		0.35
TK	**	***	***	***	***	***	***	***	

[a] EC: Electrical Conductivity; DM: Dry Matter; OM: Organic Matter; TN: Total Nitrogen; AN: Ammoniacal Nitrogen; ON: Organic Nitrogen; TP: Total phosphorus; TK: Total potassium

[b] Dark colour means r values higher than 0.70

NS: not significant; ** 0.01 ≤ p <0.001;*** 0.001≤p <0.0001

Table 5. Statistical performance[a] of different physicochemical models, using data from this study (n=126), for predicting slurry nutrient content (NT, total N; AN, Ammoniacal N; TK, total potassium; TP, total phosphorus)

Nutrient	**Reference**	**Equation**[b]	**RMSE**	**MAE**	**MEF**	**d-index**	**a**	**b**	**R^2**	**p**
			-------- kg m^{-3} ------							
TN	Moral et al. 2005	TN= 0.13EC+0.24	2.13	1.62	0.01	0.69	-0.18	1.48	0.63	<0.0001
	Martínez –Suller et al.2008	TN= 0.15EC+0.19	1.74	1.21	0.34	0.77	0.00	1.28		<0.0001
	Suresh et al. 2009	TN= $83.79EC^{1.250}$	1.37	0.95	0.59	0.89	1.09	0.81		<0.0001
AN	Moral et al. 2005	AN=0.11EC+0.10	0.77	0.58	0.68	0.90	-0.31	1.24	0.82	<0.0001
	Martínez–Suller et al.2008	AN=0.11EC+0.09	0.83	0.64	0.63	0.88	-0.30	1.27		<0.0001
	Suresh et al. 2009	AN[c]= $39.89EC^{1.343}$	0.64	0.46	0.78	0.95	0.03	1.00		<0.0001
TK[d]	Moral et al. 2005	TK=0.14EC-0.21	0.82	0.65	0.43	0.86	0.88	0.70	0.57	<0.0001
	Martínez–Suller et al.2008	TK=0.11EC+0.04	0.78	0.58	0.48	0.85	0.70	0.85		<0.0001
	Suresh et al. 2009	TK[c]=$0.60EC^2+102.6EC-196.3$	0.88	0.65	0.34	0.84	1.15	0.73		<0.0001
TP	Zhu et al. 2003	TP=0.035DM+0.01	1.20	0.94	0.15	0.82	-0.04	0.68	0.61	<0.0001
	Martínez–Suller et al.2008	TP=0.03DM+0.05	0.91	0.70	0.50	0.86	-0.07	0.84		<0.0001

[a] RMSE: root mean square error. MAE: mean absolute error. MEF: modeling efficiency. d-index: index of agreement

[b] EC expressed in dS m^{-1} and DM expressed in kg m^{-3}

[c] It is expressed in mg L^{-1}. Can be transformed to kg m^{-3} by dividing by 1000 the value obtained in the equation

[d] TK values <5 kg TK m^{-3} (n=99)

In linear regressions between simulated and observed values: intercept (a), slope (b), coefficient of determination (R^2) and signification (p)