On-farm Measurement of Electrical Conductivity for the Estimation of Ammonium Nitrogen Concentration in Pig Slurry

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ABSTRACT

Pig (*Sus scrofa domesticus*) slurry (PS) is commonly applied as fertilizer to agricultural fields. Knowledge of PS nitrogen content is essential for good management, but PS nitrogen content is highly variable, not only between farms but also within a farm. Laboratory analysis of animal slurries is often expensive and impractical for routine farmer use. Therefore, when slurry is spread on land, its fertilizer value is generally unknown, resulting in the risk of pollution. In this work, two rapid and suitable for field use methods for determining PS ammonium N (NH_4^+–N) concentration (Quantofix and conductimetry) are evaluated. The electrical conductivity of a dilution 1 PS:9 distilled water had better results than Quantofix, did not need reagents, and gave a direct value of NH_4^+–N concentrations (range, 1.0–7.6 kg NH_4^+–N m^{-3}). The conductimetry method allows the use of alternative waters with EC <1.9 dS m^{-1} for dilution. This method is being introduced to farmers in northeast Spain to improve PS management and has been well received due to its low cost and ease of use.

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Abbreviations: DM, dry matter; EC, electrical conductivity; EC$_{1:9}$, electrical conductivity dilution, 1 pig slurry:9 distilled water; EC$_w$, electrical conductivity water dilution; MAE, mean absolute error; MB, mean bias; MEF, modeling efficiency; OM, organic matter; ON, organic nitrogen; PS, pig slurry; TK, total potassium; TN, total nitrogen; TP, total phosphorus.

Introduction

Spain is the second country in Europe in pig production, with an annual average (years 2005–2010) of 26 million head (FAOSTAT, 2011). The 85 million tons of nitrogen (N) per year contained in the pig slurry (PS) produced is mainly recycled by spreading it on agricultural fields. The basis for rational management of PS as fertilizer should be agronomic optimum rather than maximum, thereby boosting mineral fertilizer savings and avoiding environmental damage as well as reducing the risk of nitrate leaching and nutrient runoff associated with high application rates (Piccinini and Bortone, 1991; Higgings et al. 2004).

Nutrient concentrations of PS present large variability, mainly depending on the type of farm; animal breed, age, diet, and management; and slurry storage method (Levasseur, 1998; Chantigny et al., 2004; Moral et al., 2005; Sánchez and González, 2005). As a first approach, standard values can provide an estimate of the nutrient content of slurries, depending on the farm type and management, even though for the same farm type and management PS nutrient content can be highly variable. The best option to ascertain nutrient content of slurry is laboratory analysis. However, this option

is not always practical because the nutrient content should be known at the time of spreading, and nutrient content can change during storage or as the slurry lagoon is emptied. Moreover, the cost of laboratory analysis is high.

Ammonium N (NH_4^+–N) is the main form of N in PS (around 70–75% of total N) (Irañeta et al., 1999; Christensen et al., 2009). When PS is applied to soil, NH_4^+–N quickly transforms to nitrate N, which is available to plants and susceptible to leaching. Organic N (ON) is only a small portion of N in PS, in contrast to other slurries and manures, and must be mineralized (i.e., converted to mineral N) before plants can use it.

Accurate estimates of total N content of PS are important, but also nutrient management plans, used to reduce nonpoint-source pollution from animal operations, require the knowledge of N availability to adjust N applications to the current legislation, such as the 170 kg N ha^{-1} equivalent of organic manure regulated in the nitrate directive (Directive 91/976/EC) for vulnerable areas. To do so, it is essential to know the PS NH_4^+–N concentration of the manure.

Various direct and indirect rapid methods for determining NH_4^+–N concentration of PS are available. Direct methods, such as Quantofix (Piccinini and Bortone, 1991; Ferrer et al., 2000; Irañeta and Abaigar, 2002), Agros (Bertrand and Smagghe, 1985; Piccinini and Bortone, 1991; Levasseur, 1998; Van Kessel and Reeves, 2000), or reflectometry (Van Kessel and Reeves, 2000, Giroux et al., 2004), directly determine NH_4^+–N concentrations. Indirect methods, such as densimetry (Tunney, 1979; Bertrand and Smagghe, 1985; Levasseur, 1998; Scotford et al., 1998; Van Kessel et al., 1999; Van Kessel and Reeves, 2000; Irañeta and Abaigar, 2002; Zhu et al., 2003) or conductimetry (Stevens et al., 1995; Levasseur, 1998; Scotford et al., 1998; Van Kessel and Reeves, 2000; Provolo and Martinez-Suller, 2007), measure a physicochemical property that is related to NH_4^+–N concentration. The measure is later transformed to NH_4^+–N concentration using a conversion or calibration equation.

These rapid methods are generally cheap and have sufficient precision for establishing the PS rate according to the NH_4^+–N concentration. These methods do have some limitations. Direct methods, such as Agros or Quantofix, need a reagent, which is corrosive and needs to be prepared each time because of degradation during storage. In addition, there is a risk of damage during handling of reagents. In the indirect methods, the reading needs to be transformed to NH_4^+–N concentration using the corresponding transformation equation, which entails risk of error. To solve these problems, we have developed a methodology for determining PS NH_4^+–N concentration based on the

reading of electrical conductivity (EC) of an appropriate slurry dilution. This methodology is rapid, easy, low cost, and robust and permits the measurements of NH_4^+–N content of PS in each vacuum tanker before being spread on fields, thereby allowing improvement of PS management by farmers.

The objectives of this work were (i) to evaluate the performance of Quantofix and conductimetry (on a 1 PS:9 distilled water [v/v] solution) for an "in field" estimation of PS NH_4^+–N concentration in an ample range of concentrations and (ii) to evaluate the effect of the salinity of the dilution water on the estimation of NH_4^+–N concentration by conductimetry.

MATERIALS AND METHODS

Description of the Methods

Quantofix-N Volumeter Method

The Quantofix method is a direct method for measuring NH_4^+–N concentrations that was developed by the German company Rimu-Luftugstecmnik and works in the range between 0 and 8 kg NH_4^+–N m^{-3}. The principle of Quantofix is the transformation of the slurry NH_4^+–N into N_2. The Quantofix reagent provided by the manufacturing company is expensive; for this reason, Piccinini and Bortone (1991) developed a cheap and easy to obtain reagent that is extensively used. It is made up of a 1:5 mixture of sodium hydroxide (40%, w/v) and sodium hypochlorite (160–180 g active Cl L^{-1}). To initiate the reaction, 150 mL of reagent is mixed with 100 mL of slurry and 200 mL distilled water to produce the following reaction:

$$3NaOCl + 2NH_4^+ + 2OH^- \rightarrow 3NaCl + 5H_2O + N_2(gas)$$
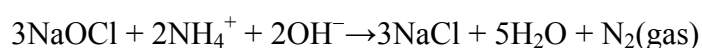
The level of the water column displaced by the N_2 produced is then read in a tube graduated in kg NH_4^+–N m^{-3}.

We estimated the error of Quantofix in measuring NH_4^+–N concentrations of standard solutions with concentrations of 2 and 4 kg NH_4^+–N m^{-3} (prepared with ammonium chloride); errors were lower than ±0.1 kg NH_4^+–N m^{-3}.

Conductimetry method

Electrical conductivity (25°C) is an indirect measurement of the total ion concentration in a solution. In samples with pH close to neutrality, such as slurry, the contribution of H^+ and OH^- ions to EC is minimal, and the EC value is ruled by the concentrations of cations and anions in solution. In slurry, the main cations are Na^+, K^+,

Ca^{2+}, Mg^{2+}, and NH_4^+, which are balanced with SO_4^{2-}, PO_4^{2-}, and Cl^- anions. The predominant cation is NH_4^+, followed by K^+ (Stevens et al., 1995); therefore, the EC could be used as an indirect measurement of the concentration of NH_4^+ in solution.

When solutions are very concentrated, the relationship between the EC and the concentration of ions in solution is not linear due to the electric and ionic interactions (i.e., ion pairing effects) between the charged ions (Sposito, 2008). To work in the linear range of the relationship between EC and the concentration of ions, a 1:9 dilution (1 part slurry and 9 parts distilled water) (Yagüe and Quílez, 2009) was made before EC measurement. Moreover, the EC of PS is high; we found values as high as 41.5 dS m^{-1}, which are not measured by all commercial EC meters. The EC readings in the 1:9 dilution (<10 dS m^{-1}) are in the range of most commercial EC meters.

Sample Collection and Measurements

Slurry samples (n = 97) were collected from tanks before spreading and from pits and storage lagoons of different pig farms (48 fattening, 43 maternity, and 6 closed cycle farms) in the Ebro River Valley in northeast Spain from 2006 to 2009. In some of the lagoons, samples were taken at different depths to determine slurry variability. We avoided farms where any type of additive was added to the slurry because the additives contain soluble salts that modify the relation between EC and NH_4^+–N concentration. Approximately 3 L of PS was collected in each sample and mixed thoroughly. Then, in situ NH_4^+–N concentration was determined using Quantofix. Care was taken that a tight seal was obtained and that the water never descended in the measuring tube. If this occurred, the analysis was repeated. We found that careful training is necessary to use Quantofix properly.

A 1:9 dilution was prepared by mixing 50 mL of PS and 450 mL of distilled water in a plastic bottle. The bottle was closed and agitated for approximately 30 s. Then EC ($EC_{1:9}$) was measured with a portable conductimeter, with a resolution of 0.01 dS m^{-1}, when the reading became stable. The portable EC meter was a large instrument, and its field use is awkward for farmers. Therefore, in the last 61 samples, the EC was also measured with a pen EC meter with a range from 0 to 10 dS m^{-1} and a resolution of 0.02 dS m^{-1}. The analyses were performed by different assistants and personnel in training and by several farmers. There was no need for specific training in the use of the EC meters, in contrast to the Quantofix method.

Samples were analyzed in the laboratory for dry matter (DM) by gravimetry at 105°C, density by gravimetry, pH by potentiometry (in a 1:5 dilution), EC at 25°C by conductimetry (the EC was measured in a 1:5 dilution in 44 PS samples), organic matter (OM) by calcination at 550°C, NH_4^+–N by the modified Kjeldhal method (Devarda without digestion), and ON by the Kjeldahl method. Total phosphorus (TP) and total potassium (TK) were analyzed with inductively coupled plasma atomic emission spectroscopy after acid digestion of slurry (USEPA, 1992).

Distilled water is not usually available on the farms, so we tested the influence of alternative types of water on the efficiency and viability of the method. We chose three types of water: two samples from irrigation ditches, the first of high salinity (I1: EC = 1.86 dS m^{-1}, Na-Ca-Cl-SO$_4$ type water) and the second of low salinity (I2: EC = 0.55 dS m^{-1}, Ca-HCO$_3$ type water), and one sample of tap water (EC = 0.84 dS m^{-1}, Ca-Na-HCO$_3$–SO$_4$–Cl type water). Thirty-two PS samples with a range of NH_4^+–N concentrations from 1.1 to 6.9 kg NH_4^+–N m^{-3} were used in this analysis. Electrical conductivity was measured in the 128 dilutions (1 PS:9 water) prepared with the 32 PS samples and the four water types (I1, I2, tap water, and distilled water).

Data Analysis

The statistical analysis was performed using the SAS statistical package (SAS Institute, 2001). The effect of farm type on the composition of the slurry, rapid method, and water dilution was evaluated by ANOVA and Duncan's multiple range test ($p \leq 0.05$).

Linear regression analysis between NH_4^+–N concentrations determined by each of the two rapid methods (independent variable) and laboratory NH_4^+–N concentrations (dependent variable) was performed. Agreement between NH_4^+–N concentrations determined by the two rapid methods (Quantofix and EC$_{1:9}$) and laboratory determinations was evaluated by the following indices: mean bias (MB, Eq. [1]), bias standard error (BSE, Eq. [2]), mean absolute error (MAE, Eq. [3]), root mean square error (RMSE, Eq. [4]), modeling efficiency statistic (MEF, Eq. [5]), and index of agreement (d, Eq. [6]).

$$MB = \frac{\sum_{i=1}^{N}(P_i - L_i)}{N} \qquad \text{[Eq. 1]}$$

$$BSE = \left[\frac{\sum_{i=1}^{N}(P_i - L_i - MB)^2 \Big/ N-1}{N} \right]^{0.5} \qquad \text{[Eq. 2]}$$

$$MAE = \left[\frac{\sum_{i=1}^{N}|P_i - L_i|}{N} \right] \qquad \text{[Eq. 3]}$$

$$RMSE = \left[\frac{\sum_{i=1}^{N}(P_i - L_i)^2}{N} \right]^{0.5} \qquad \text{[Eq. 4]}$$

$$MEF = 1 - \left[\frac{\sum_{i=1}^{N}(P_i - L_i)^2}{\sum_{i=1}^{N}(L_i - \overline{L})^2} \right] \qquad \text{[Eq. 5]}$$

$$d = 1 - \left[\frac{\sum_{i=1}^{N}(P_i - L_i)^2}{\sum_{i=1}^{N}(|P_i - \overline{L}| + |L_i - \overline{L}|)^2} \right] \qquad \text{[Eq. 6]}$$

In equations [1] through [6], L_i denotes the laboratory NH_4^+–N concentration, P_i denotes the NH_4^+–N concentration determined by Quantofix or $EC_{1:9}$ for the ith sample, n is the number of samples, and $\overline{L}$ is the average laboratory NH_4^+–N concentration.

The first two indices, MB and bias standard error, indicate if the methods give an unbiased estimation of NH_4^+–N concentrations. Mean bias is the oldest and most commonly used statistic for assessing model accuracy (Tedeschi, 2006). Root mean square error and MAE are among the best overall measures of method performance, although MAE is less sensitive to extreme values than RSME (Willmott, 1982). The MEF index defined by Tedeschi (2006) is considered by Mayer and Butler (1993) to be the best overall measure of agreement between observed and simulated values.

The relative difference measures, such as $RMSE/\overline{L}$, are unstable when $\overline{L}$ or n becomes small; therefore, Willmott (1982) defined the index of agreement that is a relative and bounded measure. Agreement between the estimation method and the

laboratory determination would improve as d and MEF approach unity and RMSE and MAE approach zero. In a perfect fit, d and MEF would result in a value equal to 1.

RESULTS

Characterization of the Slurry Samples: Variability and Relation between Parameters

We found large variability (Table 1) in the physicochemical parameters of the slurry samples, as has been widely reported in literature (Sánchez and González, 2005; Moral et al., 2005). Electrical conductivity ranged between 9.72 and 41.50 dS m^{-1} and between 1.78 and 9.02 dS m^{-1} when the EC was measured in the 1:5 dilution. Dry matter ranged between 6.89 and 238.12 kg DM m^{-3} and organic matter between 3.71 and 182.16 kg OM m^{-3} and had average values (±SD) of 53.48 (±45.73) and 37.06 (±34.17) kg m^{-3}, respectively.

The nutrient content presented even higher variability. Total N ranged from 1.42 to 10.13 kg m^{-3} and had an average value of 4.50 kg m^{-3}; NH$_4^+$–N ranged between 1.02 and 7.57 kg m^{-3}, and organic N (ON) ranged between 0.17 and 6.02 kg m^{-3}. Total P ranged between 0.05 to 6.38 kg m^{-3}, and TK ranged between 0.53 and 19.99 kg m^{-3}.

On fattening farms (>90% of total farms in Aragon), total nitrogen (TN), NH$_4^+$–N, and ON concentrations were higher than in maternity and closed cycle farms (Table 2). The average NH$_4^+$–N:TN ratio was not different between fattening farms (68%), closed cycle farms (71%), and maternity farms (75%). The NH$_4^+$–N:TN ratio has important implications because the majority of regulations, such as the nitrate directive, express N restrictions in terms of total N applied with organic sources. The coefficient to convert NH$_4^+$–N to TN on fattening farms was 1.47, similar to the value of 1.57 reported by Ziegler and Heduit (1991).

We detected a significant and strong correlation (Table 3) between OM and DM ($r = 0.99$; $p < 0.001$). The TP concentration was highly correlated to DM ($r = 0.95$; $p < 0.001$) and OM ($r = 0.94$; $p < 0.001$) because it is associated mainly with the solid fraction of PS (Sánchez and González, 2005; Christensen et al., 2009).

Ammonium N and TK concentrations were strongly correlated to EC because NH$_4^+$ and K$^+$ are the main cations in the liquid phase of PS; this result is well known in the literature (Stevens et al., 1995).

Total N was correlated significantly with EC, DM, and OM, but the strongest relationships were found with NH$_4^+$–N and ON, which indicates that the contribution of

NH_4^+–N and ON to total N is relatively constant. This ratio could be altered by different processes occurring during a prolonged storage time (i.e., sedimentation of the organic fraction or volatilization of ammonia).

Evaluation of Quantofix and Conductimetry Methods

Relationship between Quantofix and laboratory ammonium nitrogen concentrations

Quantofix NH_4^+–N concentrations were significantly related ($R^2 = 0.78$; $p < 0.001$) (Fig. 1) to laboratory NH_4^+–N concentrations, but for concentrations >5 kg NH_4^+–N m^{-3} (Fig. 1) Quantofix underestimated NH_4^+–N concentrations. In the literature, reported Quantofix values usually just reach 4 kg NH_4^+–N m^{-3} (Piccinini and Bortone, 1991; Van Kessel and Reeves, 2000), although other authors in Spain (Ferrer et al., 2000; Irañeta and Abaigar, 2002) have also found problems for NH_4^+–N concentrations >5 kg NH_4^+–N m^{-3}.

To discern whether the problem was due to the Quantofix method or to specific characteristics of the slurry, NH_4^+–N concentrations of standard ammonium chloride solutions in the range from 4 to 8 kg NH_4–N m^{-3} were prepared. Quantofix underestimated NH_4^+–N concentrations of the standard solutions for concentrations >5 kg NH_4^+–N m^{-3}. The underestimation was due to insufficient reagent to produce a complete reaction because Quantofix was able to estimate NH_4^+–N concentrations precisely when a double amount of reagent solution (300 mL) was used (Fig. 2). We advise using a double amount of reagent when slurry NH_4^+–N concentrations are suspected of being >5 kg NH_4^+–N m^{-3}.

When slurry samples with NH_4^+–N concentrations higher than 5 kg N m^{-3} are excluded from the analysis, the determination coefficient does not improve ($R^2 = 0.78$; $p < 0.001$), and, although the slope does not differ from 1, the estimated value of the intercept (0.36) differs significantly from 0. This value gives an indication of the bias of the method. When the line is forced to the origin, the estimated value of the slope (1.11) differs significantly from 1, indicating that Quantofix underestimates NH_4^+–N concentrations.

Relationship between EC$_{1:9}$ and Laboratory Ammonium Nitrogen Concentrations

A strong linear relationship ($r^2 = 0.83$; $p < 0.001$) was detected between EC$_{1:9}$ and laboratory NH_4^+–N concentrations (Fig. 3). The points were aligned along the 1:1 line,

and the fitted regression equation had an intercept that did not differ from 0 and a slope that did not differ from 1. The slope of the regression line forced to the origin (1.01) was not different from 1, indicating that the $EC_{1:9}$ equals PS NH_4^+–N concentration in the range from 1.0 to 7.6 kg NH_4^+–N m^{-3}.

The linear relationship between EC and NH_4^+–N (and also TK) concentrations has been previously reported in the literature (Scotford et al., 1998; Stevens et al., 1995; Moral et al., 2005; Provolo and Martinez-Suller, 2007), and a good fit between the variables for EC ≤40 dS m^{-1} has been obtained. Suresh et al. (2009) established an exponential relationship between EC and NH_4^+–N concentration and a quadratic relationship between EC and K concentrations for EC values in the range to 58 dS m^{-1}. Chen et al. (2009) evaluated different models reported in the literature for determining NH_4^+–N concentrations and found that only the model proposed by Scotford et al. (1998) provided satisfactory predictions for NH_4^+–N concentrations in the range to 40 dS m^{-1} (equivalent to 5.6 kg NH_4^+–N m^{-3}). The relationship between EC and solute concentration is linear for dilute solutions, but, as the solution becomes more concentrated, interactions between ions and ion-pairing alter the linear relationship (Sposito, 2008). Stevens et al. (1995) found that EC of a dilute solution of 1 PS:10 distilled water gave a more accurate prediction of NH_4^+–N concentration than EC of the raw PS. After obtaining this result, we decided to dilute PS and to look for a dilution ratio that would not need a calibration equation or conversion coefficient to obtain NH_4^+–N concentrations.

Evaluation and Comparison of the Methods

The MB of $EC_{1:9}$ (−0.06 kg N m^{-3}) was not significantly different from 0, whereas Quantofix presented a MB (−0.41 kg N m^{-3}) that was significantly different from 0. We conclude that $EC_{1:9}$ is an unbiased estimator of NH_4^+–N concentration, whereas Quantofix underestimates laboratory NH_4^+–N concentrations. When PS samples with NH_4^+–N concentrations >5 kg N m^{-3} were excluded from the analysis, Quantofix bias decreased (−0.30 kg N m^{-3}) but continued being significantly different than 0.

Mean absolute error and RMSE were higher for Quantofix (MAE, 0.49 kg NH_4^+–N m^{-3}; RMSE, 0.65 kg NH_4^+–N m^{-3}) than for $EC_{1:9}$ (MAE, 0.41 kg NH_4^+–N m^{-3}; RMSE, 0.55 kg NH_4^+–N m^{-3}) when all the samples were considered, although the values improved for Quantofix when samples with NH_4^+–N concentrations >5 kg N m^{-3} were

excluded (MAE, 0.43 kg NH_4^+–N m^{-3}; RMSE, 0.56 kg NH_4^+–N m^{-3}). Thus, the expected errors would be smaller for $EC_{1:9}$ than for Quantofix.

The modeling efficiency and the index of agreement were higher for $EC_{1:9}$ than for Quantofix for all the samples and when samples with NH_4^+–N >5 kg N m^{-3} were excluded from the analysis (Table 4). The $EC_{1:9}$ methodology is able to give values of NH_4^+–N concentrations that are more in agreement with laboratory NH_4^+–N than Quantofix.

The better performance of $EC_{1:9}$ can also be observed in the distribution of the errors. For $EC_{1:9}$, 42% of samples presented errors that were between −0.25 and 0.25 kg NH_4^+–N m^{-3}, whereas for Quantofix, only 16% of the samples presented errors in the range of −0.25 to 0.25 kg NH_4^+–N m^{-3} (Fig. 4). Furthermore, the errors for $EC_{1:9}$ were concentrated around 0, whereas errors for Quantofix are displaced to the left in relation to the bias of the method (Fig. 4).

Average estimation errors (Fig. 4) obtained in the evaluation of the method are in the range between 0.2 and 0.4 kg NH_4^+–N m^{-3}. For average PS NH_4^+–N concentration of fattening farms (average NH_4^+–N, 3.77 kg N m^{-3}), the error would be <10% and <5% in half of the cases. When the method is used to estimate NH_4^+–N concentration of maternity farms (average NH_4^+–N, 2.48 kg N m^{-3}), the average error increases to 16%. The errors are considered reasonable to estimate target PS rates adjusted to crop N needs.

Comparison of Pen Meters versus Portable Electrical Conductivity Meters

The pen EC meter was able to estimate NH_4^+–N concentrations with the same reliability as the portable EC meter (Fig. 5). Pen $EC_{1:9}$ was unbiased, as MB did not differ from 0. Pen $EC_{1:9}$ MAE (0.43 kg NH_4^+–N m^{-3}) and RMSE (0.58 kg NH_4^+–N m^{-3}) values were similar to those obtained with a portable EC meter (Table 4). Pen MEF (0.74) and d (0.93) values were high and similar to the values obtained for the portable EC meter (Table 4). These results permit the recommendation of pen EC meters to measure NH_4^+–N concentrations of slurry dilutions of 1:9 in the field. Pen EC meters are more robust than portable EC meters and are cheaper and better accepted by farmers.

Use of Alternatives to Distilled Water for the Dilution

There was a significant linear relation between $EC_{1:9}$ and NH_4^+–N concentration for each of the four different types of dilution water analyzed (Table 5). Moreover, for each type of water, the estimated value of the intercept (a; Table 5) did not differ significantly from the EC of that water (EC_w; Table 5). For that reason, we obtained the adjusted values of $EC_{1:9}$ ($EC_{1:9}^{adj}$) by subtracting the EC of the water used in the dilution (EC_w) from $EC_{1:9}$, as shown in Eq. [7].

$$EC_{1:9}^{adj} = EC_{1:9} - EC_w \hspace{4cm} [7]$$

Then the $EC_{1:9}^{adj}$ for all PS samples and types of dilution water (n = 128) were compared with NH_4^+–N concentrations. A significant linear relationship was observed between $EC_{1:9}^{adj}$ and NH_4^+–N concentrations ($R^2 = 0.95$; $p > 0.001$). The estimated values of the intercept (−0.009) did not differ from 0, and the estimated value of the slope (0.999) did not differ from 1 (Fig. 6), indicating that $EC_{1:9}^{adj}$ is an unbiased estimator of NH_4^+–N concentration. This is confirmed by the mean bias (0.01 kg NH_4^+–N m^{-3}), which did not differ significantly from zero. The MAE (0.19 kg NH_4^+–N m^{-3}) and RMSE (0.25 kg NH_4^+–N m^{-3}) values for $EC_{1:9}^{adj}$ were smaller than those obtained in the $EC_{1:9}$ evaluation, although in this case the "variability" of the samples was lower because only 32 PS samples were used versus 97 PS samples in the evaluation of the method. The modeling efficiency (0.94) and the index agreement (0.98) were better than in the evaluation of the method for the same reasons as those explained above. It is possible to use the water available on a farm to prepare the dilution if the water has an EC lower than 1.9 dS m^{-1}. In this case, it is necessary to subtract the EC of the water from the EC measured in the 1:9 dilution to obtain the NH_4^+–N concentration of the slurry.

CONCLUSIONS

Electrical conductivity ($EC_{1:9}$) measurement of PS, after dilution of 1 part pig slurry to 9 parts distilled water, has proved to be a simple, inexpensive, accurate, and robust method for measuring PS NH_4^+–N concentration across a wide range (1.0–7.6 kg NH_4^+–N m^{-3}). The $EC_{1:9}$ was an unbiased estimator of the NH_4^+–N concentrations of PS, with average estimation error given by the mean absolute error of 0.4 kg NH_4^+–N m^{-3}. The use of alternative waters for dilution, with EC up to 1.9 dS m^{-1}, was shown to allow the

successful adaptation of the methodology only to measurement of the EC of the water and subtraction of the reading from $EC_{1:9}$.

This methodology is considered a useful tool for adjusting slurry rates at the moment of spreading increasing slurry N use efficiency and diminishing the risk for nitrate leaching and greenhouse gases emission. Acceptance by pig farmers has been excellent, and Extension Services in collaboration with technicians from farmers' associations has started its implementation in the area.

ACKNOWLEDGMENTS

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Fig. 1. Relationship between Quantofix and laboratory NH_4–N concentration (***$p < 0.001$; n = 97).

Fig. 2. Ammonium concentration determined by Quantofix of standard solutions of ammonium-chloride in the range 4 to 8 kg NH_4–N m^{-3} using the customary amount of reagent and a double amount.

Fig. 3. Relationship between electrical conductivity dilution, 1 pig slurry:9 distilled water ($EC_{1:9}$; dS m^{-1}) and laboratory NH_4–N concentration (kg N m^{-3}) (***$p < 0.001$; n = 97).

Fig. 4. Distribution of errors for electrical conductivity dilution, 1 pig slurry:9 distilled water ($EC_{1:9}$, laboratory NH_4^+–N concentration) and Quantofix (Quantofix-laboratory NH_4^+–N concentration) methods.

Fig. 5. Relationship between electrical conductivity dilution, 1 pig slurry:9 distilled water ($EC_{1:9}$) values measured with portable and pen conductimeters (***$p < 0.001$; n = 61).

Fig. 6. Relationship between adjusted electrical conductivity dilution, 1 pig slurry:9 distilled water ($EC_{1:9}$) ($EC_{1:9} - EC_w$, dS m^{-1}) adjusted by the EC of the dilution water (EC_w): D (distilled water), I1 (irrigation water EC_w: 1.86 dS m^{-1}), I2 (irrigation water EC_w: 0.55 dS m^{-1}), and T (tap water EC_w: 0.84 dS m^{-1}) and laboratory NH_4^+–N concentration (***$p < 0.001$).
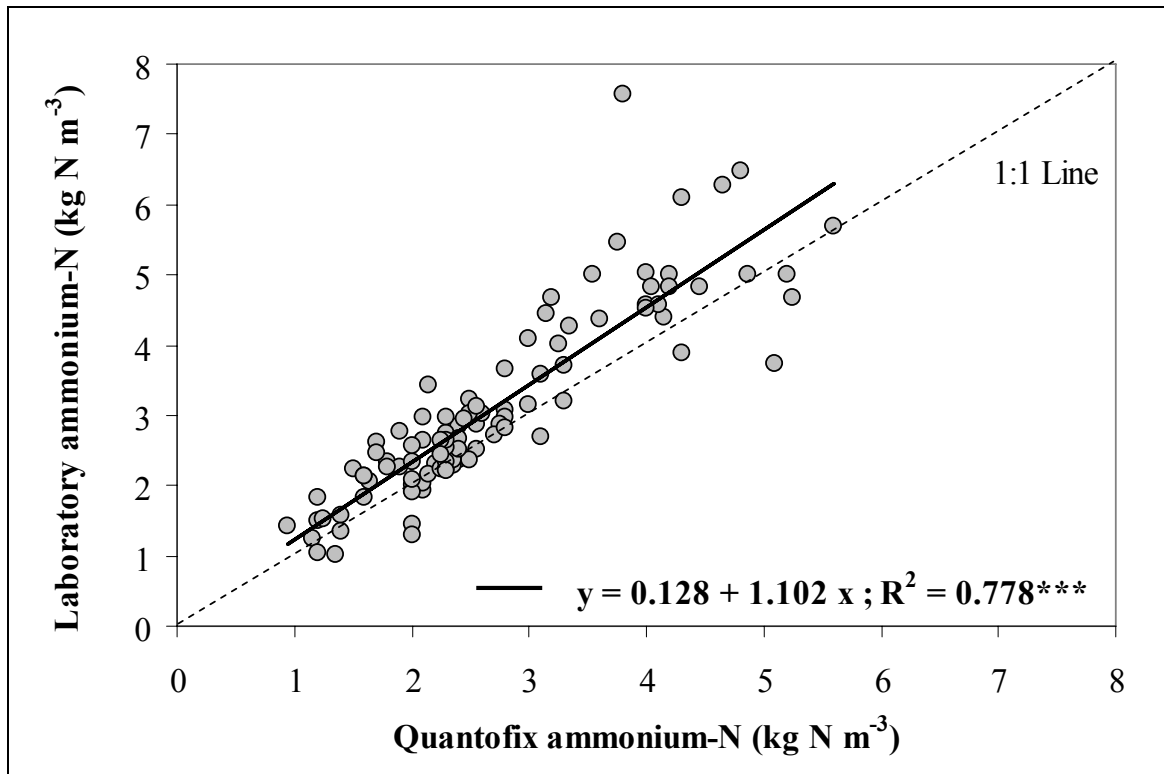
Fig. 1. Relationship between Quantofix® and laboratory ammonium-N concentration
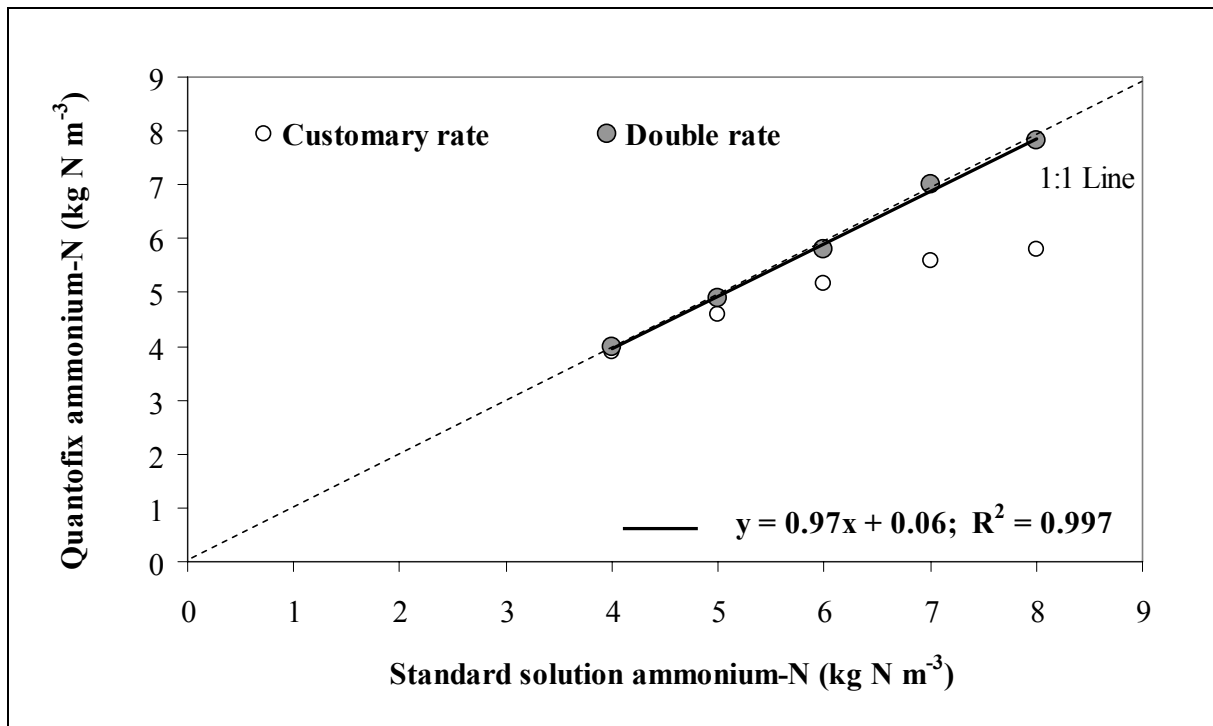
(***, p<0.001; N=97).

Fig. 2. Ammonium concentration determined by Quantofix® of standard solutions of ammonium-chloride in the range 4 to 8 kg NH_4^+-N m^{-3} using the customary amount of reagent and a double amount.
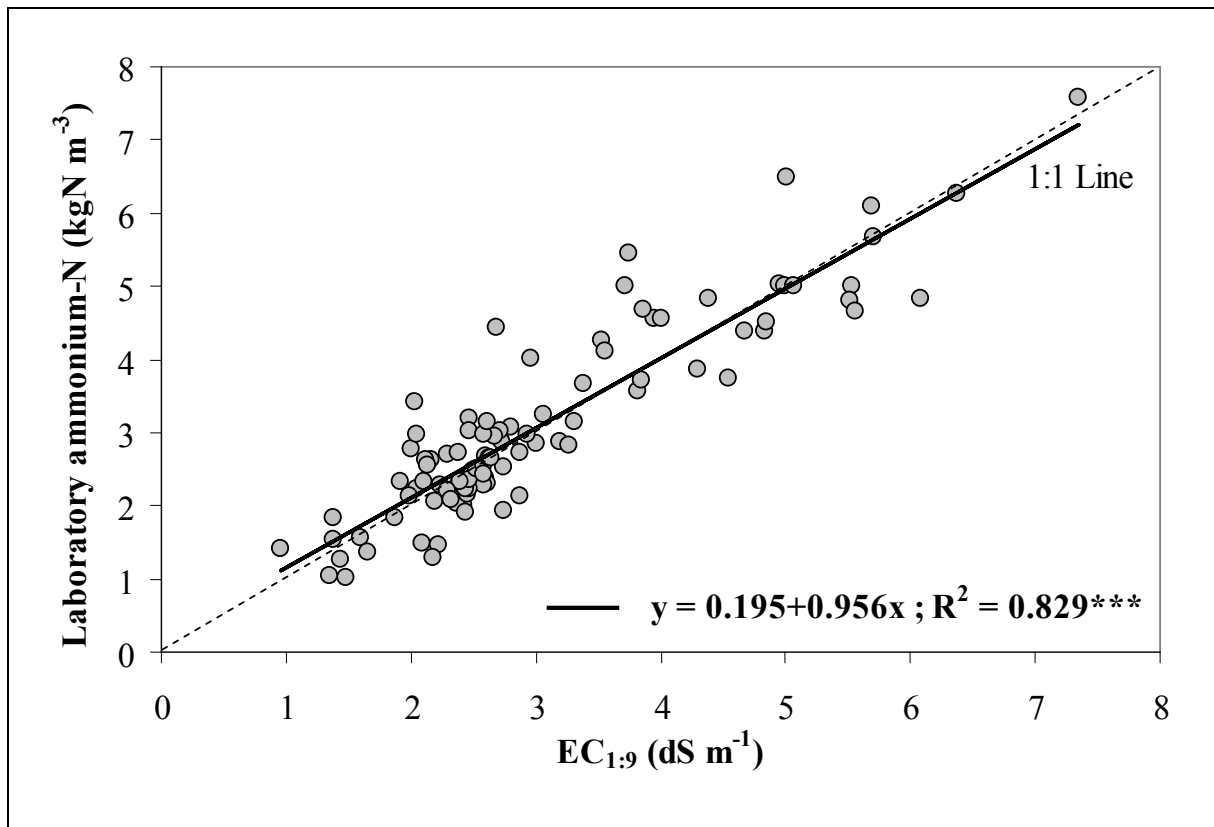
Fig. 3. Relationship between $EC_{1:9}$ (dS m^{-1}) and laboratory ammonium-N concentration (kg N m^{-3}) (***, p<0.001; N=97).
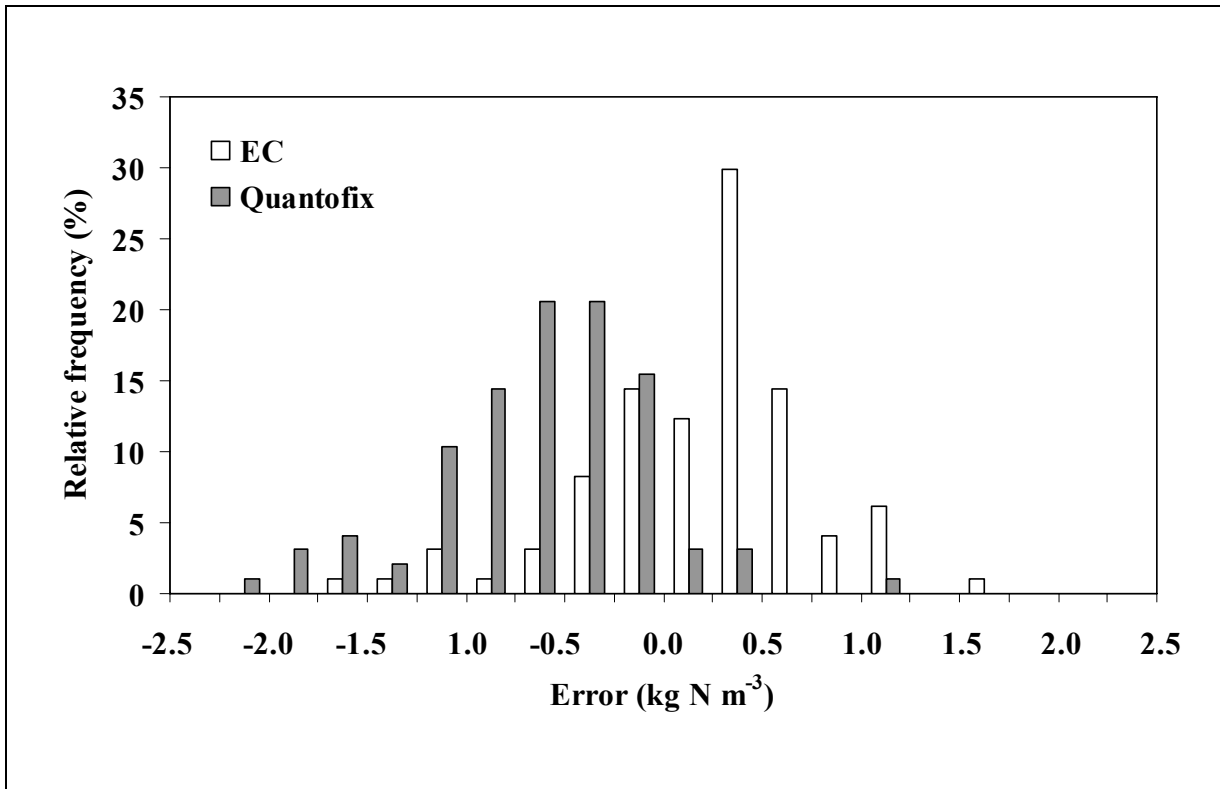
Fig. 4. Distribution of errors for $EC_{1:9}$ ($EC_{1:9}$ − laboratory NH_4^+-N concentration) and Quantofix® (Quantofix® - laboratory NH_4^+-N concentration) methods.
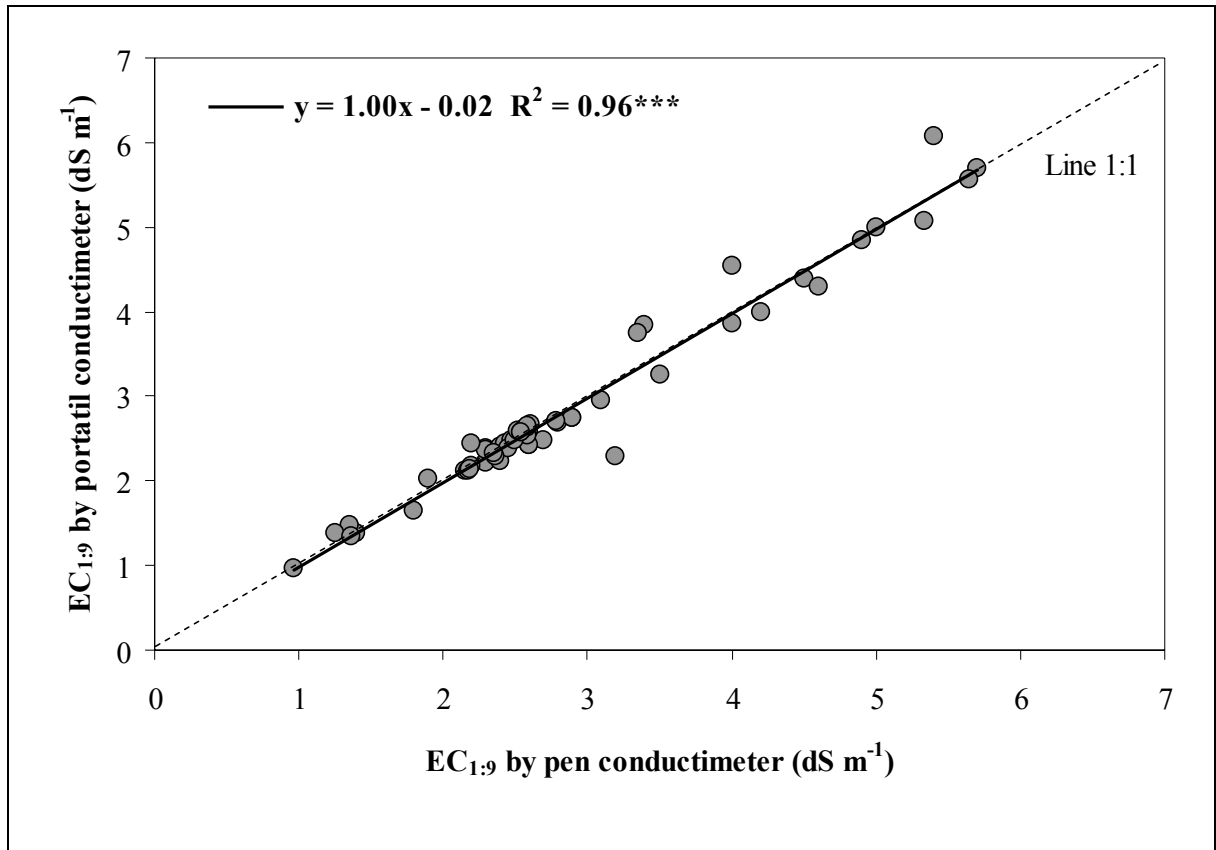
Fig. 5. Relationship between $EC_{1:9}$ values measured with portable and pen conductimeters (***p<0.0001, N=61).
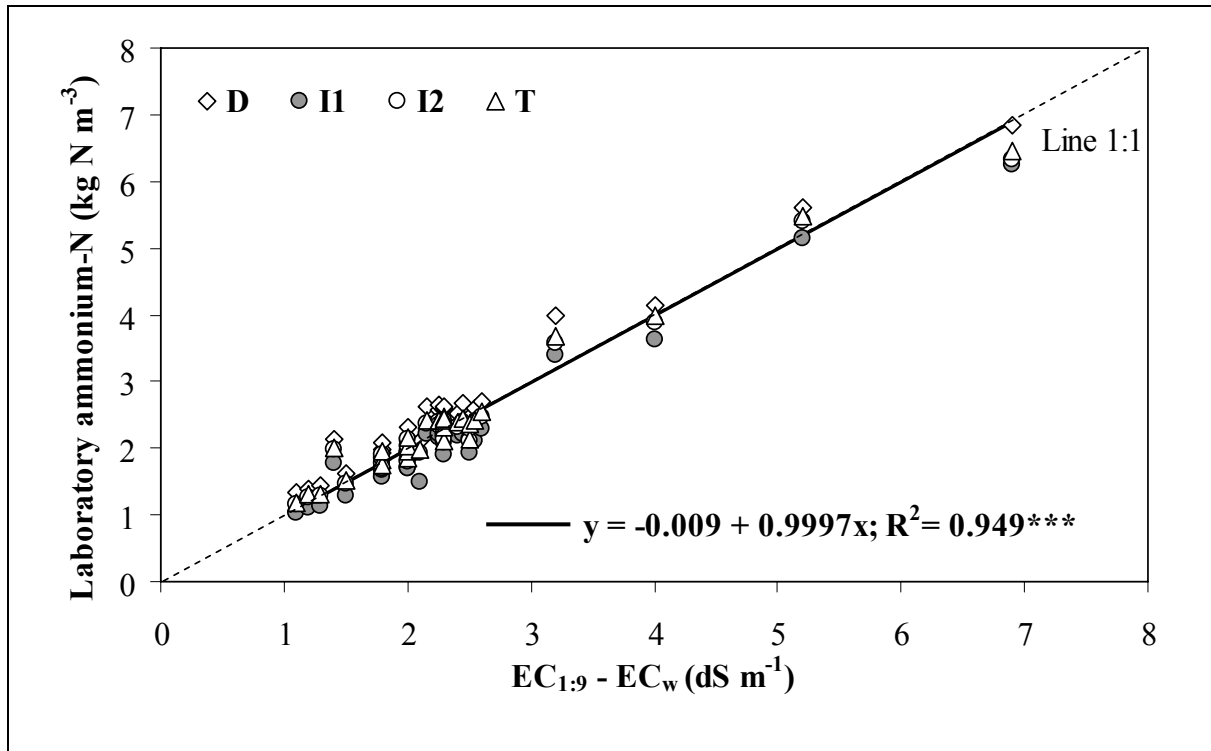
Fig. 6. Relationship between $EC_{1:9}^{adj}$ ($EC_{1:9}$ -EC_w, dS m^{-1}) adjusted by the EC of the dilution water (EC_w): D (distilled water); I1 (irrigation water EC_w: 1.86 dS m^{-1}); I2 (irrigation water EC_w: 0.55 dS m^{-1}), and T (tap water EC_w: 0.84 dS m^{-1}) and laboratory ammonium-N concentration (***, p<0.001).

Table 1. Average composition (Mean), standard deviation (SD), maximum (Max.) and minimum (Min.) values of the physicochemical parameters† of the pig slurry samples according to type of farm.

|	Total (N=97)‡				Fattening (N=48)				Maternity (N=43)				Closed Cycle (N=6)			
	Mean	Max.	Min.	SD	Mean	Max.	Min.	SD	Mean	Max.	Min.	SD	Mean	Max.	Min.	SD
$pH_{1:5}$	8.59	9.26	6.30	0.39	8.51	9.10	.7.20	0.35	8.72	9.26	8.00	0.24	8.25	8.90	6.30	0.98
Density	1035	1315	985	48.54	1058	1315	1040	60.22	1019	1077	1015	22.59	1003	1040	985	19.34
EC (dS m^{-1}) §	19.72	41.50	3.66	8.83	27.67	45.00	6.45	9.95	14.83	24.50	3.66	5.34	17.91	23.25	17.10	2.70
EC$_{1:5}$ (dS m^{-1}) ¶	4.35	9.02	1.78	1.84	5.48	10.47	1.78	2.30	3.58	6.56	2.52	0.89	nd #	nd	nd	-
DM (kg m^{-3})	53.48	238.12	6.89	45.73	71.70	238.12	8.96	52.36	36.70	129.03	6.89	24.48	27.96	62.40	18.00	2.15
OM (kg m^{-3})	37.06	182.16	3.71	34.17	49.33	182.16	5.44	38.85	25.83	97.94	3.71	29.89	19.49	44.99	11.29	17.31
TN (kg m^{-3})	4.50	10.13	1.42	2.26	5.72	10.13	1.42	2.50	3.31	7.45	1.83	1.07	3.26	5.07	2.40	0.96
NH$_4^+$-N (kg m^{-3})	3.11	7.57	1.02	1.33	3.77	7.57	1.03	1.56	2.48	3.71	1.02	0.55	2.33	3.23	1.49	0.60
ON kg m^{-3})	1.39	6.02	0.17	1.24	1.95	6.02	0.29	1.40	0.82	4.02	0.17	0.74	0.93	1.97	0.26	0.77
TP(kg m^{-3})	1.07	6.38	0.05	1.08	1.39	6.38	0.13	1.27	0.80	3.09	0.53	0.95	0.57	1.56	0.14	0.53
TK (kg m^{-3})	2.91	19.99	0.53	2.73	4.10	19.99	0.53	3.47	1.73	3.31	1.67	0.32	1.82	3.10	1.30	0.68
AN/TN	0.73	0.93	0.39	0.14	0.68	0.89	0.39	0.13	0.75	0.93	0.40	0.12	0.71	0.89	0.43	0.18

† EC Electrical Conductivity; EC$_{1:5}$: Electrical Conductivity in the dilution 1 swine slurry: 5 distilled water; DM: Dry matter; OM: Organic matter; TN: Total nitrogen; NH$_4^+$-N: Ammonium nitrogen; ON: Organic nitrogen; TP: Total phosphorus; TK: Total potassium.

‡ N: number of samples analyzed for each type of farm.

§ EC, samples analyzed N=53; fattening N=22, maternity N=18 and closed cycle N=6.

¶ EC$_{1:5}$, samples analyzed N=44; fattening N=26 and maternity N=18.

nd, no data

Table 2. Total N (NT), ammonium N (AN) and organic N (ON) in pig slurry in fattening (N=48), maternity (N=43) and closed cycle farms (N=6) and NH_4^+-N/TN ratio.

Type farm	TN	NH_4^+-N	ON	NH_4^+-N/**TN**
	--------------	**kg m^3** -----------		
Fattening	5.72	3.77	1.95	0.68
Maternity	3.31	2.48	0.82	0.75
Closed Cycle	3.26	2.33	0.93	0.71
Type farm	***	***	***	NS

NS: no significant;*** p <0.0001.

Table 3. Pearson correlation coefficients between different physicochemical parameters of the slurry for all the pig slurry samples (N=97).

	D	$EC_{1.5}$	EC	DM	OM	ON	NH_4^+-N	TN	TP	TK†
$pH_{1:5}$	-0.24NS	-0.38*	-0.08NS	-0.09NS	-0.09NS	-0.20NS	0.11NS	-0.04NS	-0.02NS	-0.03NS
D	-	-0.20NS	0.23NS	0.41***	0.39***	0.34**	0.25*	0.34***	0.32**	0.27**
$EC_{1:5}$		-	-	0.38*	0.36*	0.48**	0.86***	0.74***	0.22NS	0.75***
EC		-	-	0.27NS	0.19NS	0.45***	0.84***	0.78***	0.08NS	0.87***
DM				-	0.99***	0.93***	0.49***	0.80***	0.95***	0.57***
OM					-	0.91***	0.47***	0.78***	0.94***	0.48***
ON						-	0.89***	0.87***	0.84***	0.66***
NH_4^+-N							-	0.89***	0.35***	0.38***
TN								-	0.69***	0.58***
TP									-	0.49***
TK										-

† TK, only values $\leq$ 5 kg TK m^{-3} are considered

*, **, ***: Significant at p< 0.05; 0.01; 0.001, respectively. NS: Not significant. For abbreviations, see Table 1.

Table 4. Statistical parameters, MB: mean bias; MAE: mean absolute error: RMSE: root mean square error, MEF: modeling efficiency and d: index of agreement (N: number of samples) for the comparison between laboratory NH_4^+-N concentrations and Quantofix® and electrical conductivity ($EC_{1:9}$, 1 slurry: 9 distilled water) or adjusted EC measures ($EC_{1:9}^{adj} = EC_{1:9} - EC_w$).

	MB†	BSE	MAE	RMSE	MEF	d
	------------ kg NH_4^+-N m^{-3} ------------					
● All samples (N=97) **Range 1.02 – 7.57 kg NH_4^+-N m^{-3}**						
Quantofix®	-0.40 S	0.053	0.49	0.65	0.73	0.92
$EC_{1:9}$	-0.06 NS	0.056	0.41	0.55	0.83	0.95
● Samples < 5 kg NH_4^+-N m^{-3} (N=87) **Range 1.02 – 4.99 kg NH_4^+-N m^{-3}**						
Quantofix®	-0.31 S	0.053	0.43	0.56	0.69	0.91
$EC_{1:9}$	-0.03 NS	0.057	0.40	0.53	0.72	0.92
● Alternative dilution water (N=128) *32 PS samples, 4 types of water* **Range 1.10 – 6.90 kg NH_4^+-N m^{-3}**						
Adjusted $EC_{1:9}$, $EC_{1:9}^{adj}$	0.01 NS	0.022	0.19	0.25	0.94	0.98
● Portable *vs*. Pen EC-meter (N=61) **Range 1.02 – 5.68 kg NH_4^+-N m^{-3}**						
$EC_{1:9}$ Portable	-0.02 NS	0.074	0.42	0.57	0.75	0.93
$EC_{1:9}$ Pen	-0.01 NS	0.075	0.43	0.58	0.74	0.93

†NS: Not significantly (p>0.05) different than 0; S: Significantly (p< 0.05) different than 0.

Table 5. Electrical conductivity of the different waters tested as solvent (EC_w) and estimated parameters of the linear relation $EC_{1:9}$ (dS m^{-1}) = $a + b \cdot NH_4^+\text{-N}$ (kg N m^{-3}) with the estimation error (Error) and determination coefficient (R^2) for each of the types of water indicated in the first column.

Dilution water	EC_w (dS m^{-1})	a	b	Error (kg NH_4^+-N m^{-3})	R^2
Distilled (D)	0.00	0.24	0.98	0.21	0.97***
Irrigation 1 (I1)	1.86	1.82	0.93	0.20	0.97***
Irrigation 2 (I2)	0.55	0.71	0.95	0.20	0.97***
Tap (T)	0.84	0.95	0.93	0.20	0.97***

*** $p < 0.001$.