
M.R. Yagüe and D. Quílez. Unidad de Suelos y Riegos (Unidad asociada a EEAD-CSIC), Centro de Investigación y Tecnología Agroalimentaria de Aragón (CITA), Gobierno de Aragón. Avda. Montañana 930, 50059, Zaragoza, España.

*Corresponding author: mryague@aragon.es

Abbreviations: PS, pig slurry; NH$_4^+$-N, ammonium nitrogen; TN, total nitrogen; TK, total potassium; TP, total phosphorus; ON, organic nitrogen; DM, dry matter; OM, organic matter; EC, electrical conductivity; D, distilled water; I, irrigation water; T; tap water; EC$_{1:9}$, electrical conductivity dilution 1 PS: 9 distilled water; EC$_w$, electrical conductivity water dilution; MB, mean bias; MAE, mean absolute error; RMSE, root mean square error; MEF, modeling efficiency; d, index of agreement.
On-farm measurement of electrical conductivity for the estimation of ammonium-N concentration in pig slurry

M.R. Yagüe* and D. Quílez

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 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 (EC$_{1:9}$) had better results than Quantofix®, did not need reagents and in addition, 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. The method is being introduced to farmers in northeast Spain in order to improve PS management and has been well received due to its low cost and ease of use in practical application.

Key words: Ammonium-N; dilution-water; electrical-conductivity; rapid method; pig-slurry.
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 based on 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; Higgins et al., 2004).

Nutrient concentrations of PS present large variability, mainly depending on the type of farm, breed, age, diet, management and storage (Levasseur, 1998; Chantigny et al., 2004; Moral et al., 2005; Sánchez and Gónzalez, 2005). As a first approach, standard values can provide an estimate 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 a laboratory analysis. However, this option is not always practical, as 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 (converted to mineral N) before plants can utilize it.
Accurate estimates of total N content of PS are important, but also nutrient management plans, used to reduce non-point source pollution from animal operations require the knowledge of N availability in order 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 ammonium-N concentration of the manure.

Various direct and indirect rapid methods for determining NH₄⁺-N concentration of PS are available. Direct methods such as Quantofix® (Piccini and Bortone, 1991; Irañeta and Abaigar, 2002; Ferrer et al., 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 NH₄⁺-N concentrations. Indirect methods such as densimetry, (Tunney et al., 1975; 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 Martínez-Suller, 2007) measure a physicochemical property that is related to NH₄⁺-N concentration. The measure is later transformed to NH₄⁺-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 NH₄⁺-N concentration. These methods do exhibit 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 NH₄⁺-N concentration using the
corresponding transformation equation, which entails risk of error. To solve these
problems, we have developed a methodology for determining PS ammonium-N
concentration based on the reading of electrical conductivity (EC) of an appropriate
slurry dilution. This methodology is rapid, easy, low-cost, 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 to evaluate: i) the performance of Quantofix® and
conductimetry (on a 1:PS: 9 distilled water (v/v) solution) for an “in field” estimation of
PS ammonium-N concentration, in an ample range of concentrations and ii) 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-Luftugstecnnik 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$^{-1}$)
respectively. To initiate the reaction, 150 mL of reagent is mixed with 100 mL of slurry
and 200 mL distilled water to produce the reaction:

$$3 \text{NaOCl} + 2 \text{NH}_4^+ + 2 \text{OH}^- \rightarrow 3 \text{NaCl} + 5 \text{H}_2\text{O} + \text{N}_2 \text{(gas)}$$
The level of the water column displaced by the N\textsubscript{2} produced is then read in a tube graduated in kg NH\textsubscript{4}\textsuperscript{+}-N m\textsuperscript{-3}. We estimated the error of Quantofix\textregistered in measuring NH\textsubscript{4}\textsuperscript{+}-N concentrations of standard solutions with concentrations of 2 and 4 kg NH\textsubscript{4}\textsuperscript{+}-N m\textsuperscript{-3} (prepared with ammonium chloride); errors were lower than ±0.1 kg NH\textsubscript{4}\textsuperscript{+}-N m\textsuperscript{-3}.

Conductimetry method

Electrical conductivity (EC, 25\textdegree 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\textsuperscript{+} and OH\textsuperscript{-} 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\textsuperscript{+}, K\textsuperscript{+}, Ca\textsuperscript{+2}, Mg\textsuperscript{+2} and NH\textsubscript{4}\textsuperscript{+}, which are balanced with SO\textsubscript{4}\textsuperscript{-2}, PO\textsubscript{4}\textsuperscript{-2} and Cl\textsuperscript{-} anions. The predominant cation is NH\textsubscript{4}\textsuperscript{+} followed by K\textsuperscript{+} (Stevens et al., 1995); therefore, the EC could be used as an indirect measurement of the concentration of NH\textsubscript{4}\textsuperscript{+} 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). In order to work in the linear range of the relationship between EC and the concentration of ions, a 1:9 dilution (1 part of slurry and 9 parts of distilled water; Yagüe and Quílez, 2009) was made prior to EC measurement. Moreover, the EC of PS is high; we found values as high as 41.5 dS m\textsuperscript{-1}, which are not measured by all commercial EC-meters. The EC readings in the 1:9 dilution (< 10 dS m\textsuperscript{-1}) are in the range of most commercial EC-meters.

Sample collection and measurements
Slurry samples (n=97) were collected from tanks before spreading, pits and storage lagoons of different pig farms (48 fattening, 43 maternity, and 6 closed cycle farms) in the Ebro River Valley (Northeast Spain) from 2006-2009. In some of the lagoons samples were taken at different depths to gather slurry variability. We avoided farms where any type of additive was added to the slurry. They 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; it was closed and agitated for around 30 seconds. 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. It was apparent that the portable EC-meter was a large instrument and its field use is awkward for farmers. For that reason, 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 resolution of 0.02 dS m$^{-1}$. The analyses were performed by different assistants and personnel in training and by several farmers. It was apparent that there was no need for specific training in the use of the EC-meters (portable of pen), 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), organic N (ON) by the Kjeldahl method. Total phosphorus (TP) and total potassium (TK) were analysed 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 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 was a sample of tap water (T, 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 kg NH\(_4^+\)-N m\(^{-3}\) to 6.9 kg NH\(_4^+\)-N m\(^{-3}\) were used in this analysis.

EC was measured in the 128 dilutions (1 PS: 9 water) prepared with the 32 PS samples and the four water types (I1, I2, T and distilled).

**Data analysis**

The statistical analysis was performed using the SAS statistical package (SAS Institute, 1999-2001). The effect of farm type on the composition of the slurry, rapid method and water dilution was evaluated by analysis of variance and the Duncan 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).

\[
MB = \frac{\sum_{i=1}^{n}(P_i - L_i)}{n}
\]

[Eq. 1]

\[
BSE = \left[ \frac{\sum_{i=1}^{n}(P_i - L_i - MB)^2}{n} \right]^{0.5}
\]

[Eq. 2]

\[
MAE = \left[ \frac{\sum_{i=1}^{n}|P_i - L_i|}{N} \right]
\]

[Eq. 3]

\[
RMSE = \left[ \frac{\sum_{i=1}^{n}(P_i - L_i)^2}{N} \right]^{0.5}
\]

[Eq. 4]

\[
MEF = 1 - \frac{\sum_{i=1}^{n}(P_i - L_i)^2}{\sum_{i=1}^{n}(L_i - \overline{L})^2}
\]

[Eq. 5]

\[
d = 1 - \frac{\sum_{i=1}^{n}(P_i - L_i)^2}{\sum_{i=1}^{n}(|P_i - \overline{P}| + |L_i - \overline{L}|)^2}
\]

[Eq. 6]

In the above equations, \(L_i\) denotes the laboratory \(NH_4^+\)-N concentration and \(P_i\) the \(NH_4^+\)-N concentration determined either by Quantofix® or EC\(_{1:9}\) for the \(i^{th}\) sample, \(n\) is the number of samples, and \(\overline{L}\) is the average laboratory \(NH_4^+\)-N concentration.
The first two indices, MB and BSE, indicate if the methods give an unbiased estimation of NH$_4^+$-N concentrations. MB is the oldest and most used statistic for assessing model accuracy (Tedeschi, 2006). RMSE 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) as the best overall measure of agreement between observed and simulated values.

The relative difference measures, such as RMSE/$\bar{y}$, are unstable when $\bar{y}$ or n became 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 one.

Results and discussion

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 have been widely reported in literature (Sánchez and Góngalez, 2005; Moral et al., 2005). EC 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 (DM) 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 between 1.02 and 7.57
kg m$^{-3}$, and organic N (ON) between 0.17 and 6.02 kg m$^{-3}$. Phosphorus (TP) ranged between 0.05 to 6.38 kg m$^{-3}$ and potassium (TK) between 0.53 and 19.99 kg m$^{-3}$. On fattening farms (> 90% of total farms in Aragon), 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 (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 ($r=0.99$; $p<0.001$) and the TP concentration was highly correlated to DM ($r=0.95$, $p<0.001$) and OM ($r=0.94$, $p<0.001$), as 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, as 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 would indicate 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 AN 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 higher than 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 et al., 2002) have also found problems for NH$_4^+$-N concentrations higher than 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 larger than 5 kg NH$_4^+$-N m$^{-3}$. The underestimation was due to insufficient reagent to produce a complete reaction, as 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 higher than 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) is 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 NH$_4^+$-N concentrations
A strong linear relationship \( r^2 = 0.83, p < 0.001 \) was also 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 than 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 than 1, indicating that the EC_{1:9} equals PS ammonium-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 Martínez-Suñer, 2007), and a good fit between the variables for EC \( \leq 40 \) dS m\(^{-1}\) 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’s in the range to 58 dS m\(^{-1}\). Chen et al. (2009), evaluated different models reported in 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 1:10 (1 PS: 10 distilled water) gave a more accurate prediction of NH\(_4^+\)-N concentration than EC of the raw PS. Following this result, we decide to dilute PS and look for a dilution ratio that would not need a calibration equation or conversion coefficient to obtain NH\(_4^+\)-N concentrations.
Mean bias of EC$_{1:9}$ (-0.06 kg N m$^{-3}$) was not significantly different than zero, whereas Quantofix® presented an MB (-0.41 kg Nm$^{-3}$) that was significantly different than 0. We conclude that EC$_{1:9}$ is an unbiased estimator of NH$_4^+$-N concentration whilst 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.

MAE and RMSE were comparatively 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 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, 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$^{-3}$ whilst for Quantofix® only 16% of the samples presented errors in the range -0.25 to 0.25 kg NH$_4^+$-N m$^{-3}$ (Fig. 4). It can also be observed in Figure 4 that 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.
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 ammonium-N concentration of fattening farms (average NH$_4^+$-N = 3.77 kg N m$^{-3}$), the error would be less than 10% and less than 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$^{-3}$) average error increases to 16%. The errors are considered reasonable in order to estimate target PS rates adjusted to crop N needs.

Comparison of pen vs. portable EC-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$^{-3}$) were similar to those obtained with a portable EC-meter (Table 4). Pen MEF (0.74) and d (0.93) 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, are cheaper and are 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.

\[ EC_{1:9}^{adj} = EC_{1:9} - EC_w \]  

[Eq. 7]
Then the \( EC_{1:9}^{\text{adj}} \) for all PS samples and types of dilution water (\( N=128 \)) were compared to \( NH_4^+ \)-N concentrations. A significant linear relationship was observed between \( EC_{1:9}^{\text{adj}} \) 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 \( EC_{1:9}^{\text{adj}} \) is an unbiased estimator of \( NH_4^+ \)-N concentration.

This is confirmed by the mean bias (0.01 kg \( NH_4^+ \)-N m\(^{-3} \)) that 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 \( EC_{1:9}^{\text{adj}} \) were smaller than those obtained in the \( EC_{1:9} \) evaluation, although it has to be considered that, in this case, the “variability” of the samples was lower as 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 pig slurry (PS), after dilution 1 part pig slurry and to 9 parts distilled water, has proved to be a simple, inexpensive, accurate, and robust for measuring PS ammonium-N concentration, across a wide range (1.0 to 7.6 kg \( NH_4^+ \)-N m\(^{-3} \)). The \( EC_{1:9} \) was an unbiased estimator of \( NH_4^+ \)-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 farmers associations technicians has
started its implementation in the area.

Acknowledgements

The authors would like to thank the pig farmers for their collaboration and Miguel
Izquierdo, Jesús Gaudó and Francisco Iguácel for their invaluable field management
assistance. This study was funded by the National Institute for Agriculture and Food
Research and Technology of Spain - INIA (projects SC00-061 and RTA-2010-00126)
and with FEDER (European Fund for Regional Development) and FEADER (European
Agricultural Fund for Rural Development) funds.
References


Legend figures

Figure 1. Relationship between Quantofix® and laboratory ammonium-N concentration (***, p<0.001; n=97).

Figure 2. Ammonium concentration determined by Quantofix® of standard solutions of ammonium-chloride in the range 4 to 8 kg NH₄-N m⁻³ using the customary amount of reagent and a double amount.

Figure 3. Relationship between EC₁:₉ (dS m⁻¹) and laboratory ammonium-N concentration (kg N m⁻³) (***, p<0.001; n=97).

Figure 4. Distribution of errors for EC₁:₉ (EC₁:₉ – laboratory NH₄⁺-N concentration) and Quantofix® (Quantofix® - laboratory NH₄⁺-N concentration) methods.

Figure 5. Relationship between EC₁:₉ values measured with portable and pen conductimeters (**p<0.001, n=61).

Figure 6. Relationship between EC₉ adj (EC₁:₉ -EC₉, dS m⁻¹) adjusted by the EC of the dilution water (EC₉): D (distilled water); I1 (irrigation water EC₉: 1.86 dS m⁻¹); I2 (irrigation water EC₉: 0.55 dS m⁻¹), and T (tap water EC₉: 0.84 dS m⁻¹) and laboratory ammonium-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.

\[ y = 0.97x + 0.06; \quad R^2 = 0.997 \]
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\textsubscript{1:9} (EC\textsubscript{1:9} – laboratory NH\textsubscript{4}\textsuperscript{+}-N concentration) and Quantofix\textsuperscript{®} (Quantofix\textsuperscript{®} - laboratory NH\textsubscript{4}\textsuperscript{+}-N concentration) methods.
Fig. 5. Relationship between EC$_{1:9}$ values measured with portable and pen conductimeters (* * *p<0.001, 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.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Total (n=97)‡</th>
<th>Fattening (n=48)</th>
<th>Maternity (n=43)</th>
<th>Closed Cycle (n=6)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>Max.</td>
<td>Min.</td>
<td>SD</td>
</tr>
<tr>
<td>pH1:5</td>
<td>8.59</td>
<td>9.26</td>
<td>6.30</td>
<td>0.39</td>
</tr>
<tr>
<td>Density</td>
<td>1035</td>
<td>1315</td>
<td>985</td>
<td>48.54</td>
</tr>
<tr>
<td>EC (dS m⁻¹) §</td>
<td>19.72</td>
<td>41.50</td>
<td>3.66</td>
<td>8.83</td>
</tr>
<tr>
<td>EC1:5 (dS m⁻¹) †</td>
<td>4.35</td>
<td>9.02</td>
<td>1.78</td>
<td>1.84</td>
</tr>
<tr>
<td>DM (kg m⁻³)</td>
<td>53.48</td>
<td>238.12</td>
<td>6.89</td>
<td>45.73</td>
</tr>
<tr>
<td>OM (kg m⁻³)</td>
<td>37.06</td>
<td>182.16</td>
<td>3.71</td>
<td>34.17</td>
</tr>
<tr>
<td>TN (kg m⁻³)</td>
<td>4.50</td>
<td>10.13</td>
<td>1.42</td>
<td>2.26</td>
</tr>
<tr>
<td>NH₄⁺-N (kg m⁻³)</td>
<td>3.11</td>
<td>7.57</td>
<td>1.02</td>
<td>1.33</td>
</tr>
<tr>
<td>ON kg m⁻³</td>
<td>1.39</td>
<td>6.02</td>
<td>0.17</td>
<td>1.24</td>
</tr>
<tr>
<td>TP (kg m⁻³)</td>
<td>1.07</td>
<td>6.38</td>
<td>0.05</td>
<td>1.08</td>
</tr>
<tr>
<td>TK (kg m⁻³)</td>
<td>2.91</td>
<td>19.99</td>
<td>0.53</td>
<td>2.73</td>
</tr>
<tr>
<td>NH₄⁺-N / TN</td>
<td>0.73</td>
<td>0.93</td>
<td>0.39</td>
<td>0.14</td>
</tr>
</tbody>
</table>

† EC Electrical Conductivity; EC₁:5: Electrical Conductivity in the dilution 1 pig slurry: 5 distilled water; DM: Dry matter; OM: Organic matter; TN: Total nitrogen; NH₄⁺-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 nN=53; fattening n=22, maternity n=18 and closed cycle n=6.

¶ EC₁:5, 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.

<table>
<thead>
<tr>
<th>Type farm</th>
<th>TN kg m$^3$</th>
<th>NH$_4^+$-N kg m$^3$</th>
<th>ON kg m$^3$</th>
<th>NH$_4^+$-N/TN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fattening</td>
<td>5.72</td>
<td>3.77</td>
<td>1.95</td>
<td>0.68</td>
</tr>
<tr>
<td>Maternity</td>
<td>3.31</td>
<td>2.48</td>
<td>0.82</td>
<td>0.75</td>
</tr>
<tr>
<td>Closed cycle</td>
<td>3.26</td>
<td>2.33</td>
<td>0.93</td>
<td>0.71</td>
</tr>
</tbody>
</table>

Type farm: *** *** *** NS

NS: not significant (p> 0.05); *** p <0.001.
Table 3. Pearson correlation coefficients between different physicochemical parameters of the slurry for all the pig slurry samples (n=97).

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

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

*, **, ***: Significant at p< 0.05; 0.01; 0.001, respectively. NS: not significant (p>0.05). 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$_w$).

<table>
<thead>
<tr>
<th></th>
<th>MB†</th>
<th>BSE</th>
<th>MAE</th>
<th>RMSE</th>
<th>MEF</th>
<th>d</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>kg NH$_4^+$-N m$^{-3}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>All samples</strong> (n=97)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Range: 1.02 – 7.57 kg NH$_4^+$-N m$^{-3}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Quantofix®</td>
<td>-0.40 S</td>
<td>0.053</td>
<td>0.49</td>
<td>0.65</td>
<td>0.73</td>
<td>0.92</td>
</tr>
<tr>
<td>EC$_{1:9}$</td>
<td>-0.06 NS</td>
<td>0.056</td>
<td>0.41</td>
<td>0.55</td>
<td>0.83</td>
<td>0.95</td>
</tr>
</tbody>
</table>

|                |     |      |      |      |      |      |
| **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 significant (p>0.05) different than 0; S: significant (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*NH$_4^+$-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.

<table>
<thead>
<tr>
<th>Dilution water</th>
<th>EC$_w$ (dS m$^{-1}$)</th>
<th>a</th>
<th>b</th>
<th>Error (kg NH$_4^+$-N m$^{-3}$)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distilled (D)</td>
<td>0.00</td>
<td>0.24</td>
<td>0.98</td>
<td>0.21</td>
<td>0.97***</td>
</tr>
<tr>
<td>Irrigation 1 (I1)</td>
<td>1.86</td>
<td>1.82</td>
<td>0.93</td>
<td>0.20</td>
<td>0.97***</td>
</tr>
<tr>
<td>Irrigation 2 (I2)</td>
<td>0.55</td>
<td>0.71</td>
<td>0.95</td>
<td>0.20</td>
<td>0.97***</td>
</tr>
<tr>
<td>Tap (T)</td>
<td>0.84</td>
<td>0.95</td>
<td>0.93</td>
<td>0.20</td>
<td>0.97***</td>
</tr>
</tbody>
</table>

*** p<0.001.