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15 Abbreviations: PS, pig slurry; NH_4^+-N, ammonium nitrogen; TN, total nitrogen; TK,

16 total potassium; TP, total phosphorus; ON, organic nitrogen; DM, dry matter; OM,

17 organic matter; EC, electrical conductivity; D, distilled water; I, irrigation water; T; tap

18 water; $EC_{1:9}$, electrical conductivity dilution 1 PS: 9 distilled water; EC_w, electrical

19 conductivity water dilution; MB, mean bias; MAE, mean absolute error; RMSE, root

20 mean square error; MEF, modeling efficiency; d, index of agreement.

1 **On-farm measurement of electrical conductivity for the estimation of ammonium-**

2 **N concentration in pig slurry**

3

4 **M.R. Yagüe* and D. Quílez**

5 **Abstract**

6 Pig (*Sus scrofa domesticus*) slurry (PS) is commonly applied as fertilizer to agricultural

7 fields. Knowledge of PS nitrogen content is essential for good management, but PS

8 nitrogen content is highly variable not only between farms but also within a farm.

9 Laboratory analysis of animal slurries is often expensive and impractical for routine

10 farmer use. Therefore, when slurry is spread on land its fertilizer value is generally

11 unknown resulting in risk of pollution. In this work, two rapid and suitable for field use,

12 methods for determining PS ammonium-N (NH_4^+-N) concentration (Quantofix® and

13 conductimetry) are evaluated. The electrical conductivity of a dilution 1 PS: 9 distilled

14 water ($EC_{1:9}$) had better results than Quantofix®, did not need reagents and in addition,

15 gave a direct value of NH_4^+-N concentrations (range 1.0 - 7.6 kg NH_4^+-N m^{-3}). The

16 conductimetry method allows the use of alternative waters with EC < 1.9 dS m^{-1} for

17 dilution. The method is being introduced to farmers in northeast Spain in order to

18 improve PS management and has been well received due to its low cost and ease of use

19 in practical application.

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21 **Key words:** Ammonium-N; dilution-water; electrical-conductivity; rapid method; pig-

22 slurry.

1 Introduction

2 Spain is the second country in Europe in pig production, with an annual average (years

3 2005-2010) of 26 million head (FAOSTAT, 2011). The 85 million tons of nitrogen (N)

4 per year contained in the pig slurry (PS) produced is mainly recycled by spreading it on

5 agricultural fields. The basis for rational management of PS as fertilizer should be based

6 on agronomic optimum rather than maximum, thereby boosting mineral fertilizer

7 savings and avoiding environmental damage, as well as reducing the risk of nitrate

8 leaching and nutrient runoff associated with high application rates (Piccinini and

9 Bortone, 1991; Higgins et al., 2004).

10 Nutrient concentrations of PS present large variability, mainly depending on the type of

11 farm, breed, age, diet, management and storage (Levasseur, 1998; Chantigny et al.,

12 2004; Moral et al., 2005; Sánchez and Gónzalez, 2005). As a first approach, standard

13 values can provide an estimate the nutrient content of slurries, depending on the farm

14 type and management, even though for the same farm type and management, PS

15 nutrient content can be highly variable. The best option to ascertain nutrient content of

16 slurry is a laboratory analysis. However, this option is not always practical, as the

17 nutrient content should be known at the time of spreading, and nutrient content can

18 change during storage or as the slurry lagoon is emptied; moreover, the cost of

19 laboratory analysis is high.

20 Ammonium-N (NH_4^+-N) is the main form of N in PS (around 70-75% of total N, Irañeta

21 et al., 1999; Christensen et al., 2009). When PS is applied to soil, NH_4^+-N quickly

22 transforms to nitrate-N, which is available to plants and susceptible to leaching. Organic

23 N (ON) is only a small portion of N in PS, in contrast to other slurries and manures, and

24 must be mineralized (converted to mineral N) before plants can utilize it.

1   Accurate estimates of total N content of PS are important, but also nutrient management

2   plans, used to reduce non-point source pollution from animal operations require the

3   knowledge of N availability in order to adjust N applications to the current legislation,

4   such as the 170 kg N ha^{-1} equivalent of organic manure regulated in the nitrate directive

5   (Directive 91/976/EC) for vulnerable areas. To do so, it is essential to know the PS

6   ammonium-N concentration of the manure.

7   Various direct and indirect rapids methods for determining NH_4^+-N concentration of PS

8   are available. Direct methods such as Quantofix® (Piccini and Bortone, 1991; Irañeta

9   and Abaigar, 2002; Ferrer et al., 2002), Agros® (Bertrand and Smagghe, 1985;

10   Piccinini and Bortone, 1991; Levasseur, 1998; Van Kessel and Reeves, 2000), or

11   reflectometry (Van Kessel and Reeves, 2000, Giroux et al., 2004) directly determine

12   NH_4^+-N concentrations. Indirect methods such as densimetry, (Tunney et al., 1975;

13   Bertrand and Smagghe, 1985; Levasseur, 1998; Scotford, et al., 1998; Van Kessel et al.,

14   1999; Van Kessel and Reeves, 2000; Irañeta and Abaigar, 2002; Zhu, et al., 2003) or

15   conductimetry (Stevens et al., 1995; Levasseur, 1998; Scotford, et al., 1998; Van Kessel

16   and Reeves, 2000; Provolo and Martínez-Suller, 2007) measure a physicochemical

17   property that is related to NH_4^+-N concentration. The measure is later transformed to

18   NH_4^+-N concentration using a conversion or calibration equation.

19   These rapid methods are generally cheap and have sufficient precision for establishing

20   the PS rate according to the NH_4^+-N concentration. These methods do exhibit some

21   limitations. Direct methods, such as Agros® or Quantofix®, need a reagent, which is

22   corrosive and needs to be prepared each time, (because of degradation during storage).

23   In addition, there is a risk of damage during handling of reagents. In the indirect

24   methods, the reading needs to be transformed to NH_4^+-N concentration using the

1   corresponding transformation equation, which entails risk of error. To solve these

2   problems, we have developed a methodology for determining PS ammonium-N

3   concentration based on the reading of electrical conductivity (EC) of an appropriate

4   slurry dilution. This methodology is rapid, easy, low-cost, robust, and permits the

5   measurements of NH_4^+-N content of PS in each vacuum tanker before being spread on

6   fields, thereby allowing improvement of PS management by farmers.

7   The objectives of this work were to evaluate: i) the performance of Quantofix® and

8   conductimetry (on a 1 PS: 9 distilled water (v/v) solution) for an "in field" estimation of

9   PS ammonium-N concentration, in an ample range of concentrations and ii) the effect of

10   the salinity of the dilution water on the estimation of NH_4^+-N concentration by

11   conductimetry.

12   **Materials and methods**

13   **Description of the methods**

14   Quantofix®-N Volumeter method

15   The Quantofix® method is a direct method for measuring NH_4^+-N concentrations that

16   was developed by the German Company Rimu-Luftugstecmnik and works in the range

17   between 0 and 8 kg NH_4^+-N m^{-3}. The principle of Quantofix® is the transformation of

18   the slurry NH_4^+-N into N_2. The Quantofix® reagent provided by the manufacturing

19   company is expensive; for this reason, Piccinini and Bortone (1991) developed a cheap

20   and easy to obtain reagent that is extensively used. It is made up of a 1:5 mixture of

21   sodium hydroxide (40%, w/v) and sodium hypochlorite (160-180 g active Cl L^{-1})

22   respectively. To initiate the reaction, 150 mL of reagent is mixed with 100 mL of slurry

23   and 200 mL distilled water to produce the reaction:

24   $$3\,NaOCl + 2\,NH_4^+ + 2\,OH^- \longrightarrow 3\,NaCl + 5\,H_2O + N_2\,(gas)$$
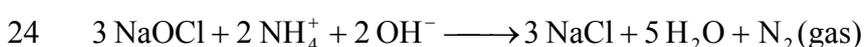
1   The level of the water column displaced by the N_2 produced is then read in a tube

2   graduated in kg NH_4^+-N m^{-3}.

3   We estimated the error of Quantofix® in measuring NH_4^+-N concentrations of standard

4   solutions with concentrations of 2 and 4 kg NH_4^+-N m^{-3} (prepared with ammonium

5   chloride); errors were lower than ±0.1 kg NH_4^+-N m^{-3}.

6   Conductimetry method

7   Electrical conductivity (EC, 25ºC) is an indirect measurement of the total ion

8   concentration in a solution. In samples with pH close to neutrality, such as slurry, the

9   contribution of H^+ and OH^- ions to EC is minimal and the EC value is ruled by the

10   concentrations of cations and anions in solution. In slurry, the main cations are Na^+, K^+,

11   Ca^{+2}, Mg^{+2} and NH_4^+, which are balanced with SO_4^{-2}, PO_4^{-2} and Cl^- anions. The

12   predominant cation is NH_4^+ followed by K^+ (Stevens et al., 1995); therefore, the EC

13   could be used as an indirect measurement of the concentration of NH_4^+ in solution.

14   When solutions are very concentrated, the relationship between the EC and the

15   concentration of ions in solution is not linear due to the electric and ionic interactions

16   (i.e., ion pairing effects) between the charged ions (Sposito, 2008). In order to work in

17   the linear range of the relationship between EC and the concentration of ions, a 1:9

18   dilution (1 part of slurry and 9 parts of distilled water; Yagüe and Quílez, 2009) was

19   made prior to EC measurement. Moreover, the EC of PS is high; we found values as

20   high as 41.5 dS m^{-1}, which are not measured by all commercial EC-meters. The EC

21   readings in the 1:9 dilution (< 10 dS m^{-1}) are in the range of most commercial EC-

22   meters.

23   **Sample collection and measurements**

1 Slurry samples (n=97) were collected from tanks before spreading, pits and storage

2 lagoons of different pig farms (48 fattening, 43 maternity, and 6 closed cycle farms) in

3 the Ebro River Valley (Northeast Spain) from 2006-2009. In some of the lagoons

4 samples were taken at different depths to gather slurry variability. We avoided farms

5 where any type of additive was added to the slurry. They contain soluble salts that

6 modify the relation between EC and NH_4^+-N concentration. Approximately 3 L of PS

7 was collected in each sample and mixed thoroughly. Then, *in situ* NH_4^+-N concentration

8 was determined using Quantofix®. Care was taken that a tight seal was obtained and

9 that the water never descended in the measuring tube. If this occurred, the analysis was

10 repeated. We found that careful training is necessary to use Quantofix® properly.

11 A 1:9 dilution was prepared by mixing 50 mL of PS and 450 mL of distilled water in a

12 plastic bottle; it was closed and agitated for around 30 seconds. Then EC ($EC_{1:9}$) was

13 measured with a portable conductimeter, with a resolution of 0.01 dS m^{-1}, when the

14 reading became stable. It was apparent that the portable EC-meter was a large

15 instrument and its field use is awkward for farmers. For that reason, in the last 61

16 samples, the EC was also measured with a pen EC-meter with a range from 0 to 10 dS

17 m^{-1} and resolution of 0.02 dS m^{-1}. The analyses were performed by different assistants

18 and personnel in training and by several farmers. It was apparent that there was no need

19 for specific training in the use of the EC-meters (portable of pen), in contrast to the

20 Quantofix® method.

21 Samples were analyzed in the laboratory for dry matter (DM) by gravimetry at 105ºC,

22 density by gravimetry, pH by potentiometry (in a 1:5 dilution), EC at 25ºC by

23 conductimetry (the EC was measured in a 1:5 dilution in 44 PS samples), organic matter

24 (OM) by calcination at 550ºC, NH_4^+-N by the modified Kjeldhal method (Devarda

1 without digestion), organic N (ON) by the Kjeldahl method. Total phosphorus (TP) and

2 total potassium (TK) were analysed with inductively coupled plasma atomic emission

3 spectroscopy after acid digestion of slurry (USEPA, 1992).

4 Distilled water is not usually available on the farms, so we tested the influence of

5 alternative types of water on the efficiency and viability of the method. We chose three

6 types of water: two from irrigation ditches, the first of high salinity (I1, EC=1.86 dS m$^-$

7 ^{1}, Na-Ca-Cl-SO$_4$ type water) and the second of low salinity (I2, EC=0.55 dS m^{-1}, Ca-

8 HCO$_3$ type water), and one was a sample of tap water (T, EC=0.84 dS m^{-1}, Ca-Na-

9 HCO$_3$-SO$_4$-Cl type water). Thirty two PS samples with a range of NH$_4^+$-N

10 concentrations from 1.1 kg NH$_4^+$-N m^{-3} to 6.9 kg NH$_4^+$-N m^{-3} were used in this analysis.

11 EC was measured in the 128 dilutions (1 PS: 9 water) prepared with the 32 PS samples

12 and the four water types (I1, I2, T and distilled).

13 **Data analysis**

14 The statistical analysis was performed using the SAS statistical package (SAS Institute,

15 1999-2001). The effect of farm type on the composition of the slurry, rapid method and

16 water dilution was evaluated by analysis of variance and the Duncan multiple range test

17 (p≤ 0.05).

18 Linear regression analysis between NH$_4^+$-N concentrations determined by each of the

19 two rapid methods (independent variable) and laboratory NH$_4^+$-N concentrations

20 (dependent variable) was performed. Agreement between NH$_4^+$-N concentrations

21 determined by the two rapid methods (Quantofix® and EC$_{1:9}$) and laboratory

22 determinations was evaluated by the following indices: mean bias (MB, Eq. 1), bias

23 standard error (BSE, Eq. 2), mean absolute error (MAE, Eq. 3), root mean square error

1 (RMSE, Eq. 4), modeling efficiency statistic (MEF, Eq. 5); and index of agreement (d,

2 Eq. 6).

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

3 [Eq. 1]

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

4 [Eq. 2]

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

5 [Eq. 3]

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

6 [Eq. 4]

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

7 [Eq. 5]

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

8 [Eq. 6]

9 In the above equations, L_i denotes the laboratory NH_4^+-N concentration and P_i the

10 NH_4^+-N concentration determined either by Quantofix® or $EC_{1:9}$ for the *i*th sample, n is

11 the number of samples, and $\overline{L}$ is the average laboratory NH_4^+-N concentration.

1 The first two indices, MB and BSE, indicate if the methods give an unbiased estimation

2 of NH_4^+-N concentrations. MB is the oldest and most used statistic for assessing model

3 accuracy (Tedeschi, 2006). RMSE and MAE are among the best overall measures of

4 method performance, although MAE is less sensitive to extreme values than RSME

5 (Willmott, 1982).

6 The MEF index defined by Tedeschi (2006) is considered by Mayer and Butler (1993)

7 as the best overall measure of agreement between observed and simulated values.

8 The relative difference measures, such as RMSE/$\overline{L}$, are unstable when $\overline{L}$ or n became

9 small; therefore, Willmott (1982) defined the index of agreement that is a relative and

10 bounded measure. Agreement between the estimation method and the laboratory

11 determination would improve as d and MEF approach unity and RMSE and MAE

12 approach zero. In a perfect fit, d and MEF would result in a value equal to one.

13 **Results and discussion**

14 **Characterization of the slurry samples: variability and relation between**

15 **parameters**

16 We found large variability (Table 1) in the physicochemical parameters of the slurry

17 samples as have been widely reported in literature (Sánchez and Gónzalez, 2005; Moral

18 et al., 2005). EC ranged between 9.72 and 41.50 dS m^{-1} and between 1.78 and 9.02 dS

19 m^{-1} when the EC was measured in the 1:5 dilution. Dry matter (DM) ranged between

20 6.89 and 238.12 kg DM m^{-3} and organic matter between 3.71 and 182.16 kg OM m^{-3}

21 and had average values (±SD) of 53.48 (±45.73) and 37.06 (±34.17) kg m^{-3} respectively.

22 The nutrient content presented even higher variability. Total N ranged from 1.42 to

23 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

1   kg m^{-3}, and organic N (ON) between 0.17 and 6.02 kg m^{-3}. Phosphorus (TP) ranged

2   between 0.05 to 6.38 kg m^{-3} and potassium (TK) between 0.53 and 19.99 kg m^{-3}.

3   On fattening farms (> 90% of total farms in Aragon), TN, NH_4^+-N, and ON

4   concentrations were higher than in maternity and closed cycle farms (Table 2). The

5   average NH_4^+-N/TN ratio was not different between fattening farms (68%), closed cycle

6   (71%) and maternity farms (75%). The NH_4^+-N/TN ratio has important implications,

7   because the majority of regulations, such as the nitrate directive, express N restrictions

8   in terms of total N applied with organic sources. The coefficient to convert NH_4^+-N to

9   TN on fattening farms was 1.47, similar to the value of (1.57) reported by Ziegler and

10   Heduit (1991).

11   We detected a significant and strong correlation (Table 3) between OM and DM

12   (r=0.99; p<0.001) and the TP concentration was highly correlated to DM (r=0.95,

13   p<0.001) and OM (r=0.94, p<0.001), as it is associated mainly with the solid fraction of

14   PS (Sánchez and González, 2005; Christensen et al., 2009).

15   Ammonium-N and TK concentrations were strongly correlated to EC, as NH_4^+ and K^+

16   are the main cations in the liquid phase of PS; this result is well known in the literature

17   (Stevens et al., 1995).

18   Total N was correlated significantly with EC, DM and OM, but the strongest

19   relationships were found with NH_4^+-N and ON, which would indicate that the

20   contribution of NH_4^+-N and ON to total N is relatively constant. This ratio could be

21   altered by different processes occurring during a prolonged storage time (i.e.

22   sedimentation of the organic fraction or volatilization of ammonia).

23   **Evaluation of Quantofix® and conductimetry methods**

24   Relationship between Quantofix® and laboratory AN concentrations

1   Quantofix® NH_4^+-N concentrations were significantly related ($R^2 = 0.78$, p<0.001, Fig.

2   1) to laboratory NH_4^+-N concentrations, but for concentrations higher than 5 kg NH_4^+-N

3   m^{-3}, (Fig. 1) Quantofix® underestimated NH_4^+-N concentrations. In the literature,

4   reported Quantofix® values usually just reach 4 kg NH_4^+-N m^{-3} (Piccinini and Bortone,

5   1991; Van Kessel and Reeves, 2000), although other authors in Spain (Ferrer et al.,

6   2000; Irañeta et al., 2002) have also found problems for NH_4^+-N concentrations higher

7   than 5 kg NH_4^+-N m^{-3}.

8   To discern whether the problem was due to the Quantofix® method or to specific

9   characteristics of the slurry, NH_4^+-N concentrations of standard ammonium chloride

10   solutions in the range from 4 to 8 kg NH_4^+-N m^{-3} were prepared. Quantofix®

11   underestimated NH_4^+-N concentrations of the standard solutions for concentrations

12   larger than 5 kg NH_4^+-N m^{-3}. The underestimation was due to insufficient reagent to

13   produce a complete reaction, as Quantofix® was able to estimate NH_4^+-N

14   concentrations precisely when a double amount of reagent solution (300 mL) was used

15   (Fig. 2). We advise using a double amount of reagent when slurry NH_4^+-N

16   concentrations are suspected of being higher than 5 kg NH_4^+-N m^{-3}.

17   When slurry samples with NH_4^+-N concentrations higher than 5 kg N m^{-3} are excluded

18   from the analysis, the determination coefficient does not improve ($R^2 = 0.78$, p<0.001)

19   and although the slope does not differ from 1, the estimated value of the intercept (0.36)

20   is differs significantly from 0. This value gives an indication of the bias of the method.

21   When the line is forced to the origin, the estimated value of the slope (1.11) differs

22   significantly from 1, indicating that Quantofix® underestimates NH_4^+-N concentrations.

23   Relationship between $EC_{1:9}$ and laboratory NH_4^+-N concentrations

1 A strong linear relationship (r^2=0.83, p<0.001) was also detected between $EC_{1:9}$ and

2 laboratory NH_4^+-N concentrations (Fig. 3). The points were aligned along the 1:1 line

3 and the fitted regression equation had an intercept that did not differ than 0 and a slope

4 that did not differ from 1. The slope of the regression line forced to the origin (1.01)

5 was not different than 1, indicating that the $EC_{1:9}$ equals PS ammonium-N concentration

6 in the range from 1.0 to 7.6 kg NH_4^+-N m^{-3}.

7 The linear relationship between EC and NH_4^+-N (and also TK) concentrations has been

8 previously reported in the literature (Scotford et al., 1998; Stevens et al., 1995; Moral et

9 al., 2005; Provolo and Martínez-Suñer, 2007), and a good fit between the variables for

10 $EC \leq 40$ dS m^{-1} obtained. Suresh et al. (2009) established an exponential relationship

11 between EC and NH_4^+-N concentration, and a quadratic relationship between EC and K

12 concentrations for EC's in the range to 58 dS m^{-1}. Chen et al. (2009), evaluated different

13 models reported in literature for determining NH_4^+-N concentrations and found that

14 only the model proposed by Scotford et al. (1998) provided satisfactory predictions for

15 NH_4^+-N concentrations in the range to 40 dS m^{-1} (equivalent to 5.6 kg NH_4^+-N m^{-3}). The

16 relationship between EC and solute concentration is linear for dilute solutions, but as

17 the solution becomes more concentrated, interactions between ions and ion-pairing alter

18 the linear relationship (Sposito, 2008). Stevens et al. (1995) found that EC of a dilute

19 solution 1:10 (1 PS: 10 distilled water) gave a more accurate prediction of NH_4^+-N

20 concentration than EC of the raw PS. Following this result, we decide to dilute PS and

21 look for a dilution ratio that would not need a calibration equation or conversion

22 coefficient to obtain NH_4^+-N concentrations.

23 Evaluation and comparison of the methods

1   Mean bias of $EC_{1:9}$ (-0.06 kg N m^{-3}) was not significantly different than zero, whereas

2   Quantofix® presented an MB (-0.41 kg Nm^{-3}) that was significantly different than 0.

3   We conclude that $EC_{1:9}$ is an unbiased estimator of NH_4^+-N concentration whilst

4   Quantofix® underestimates laboratory NH_4^+-N concentrations. When PS samples with

5   NH_4^+-N concentrations > 5 kg N m^{-3} were excluded from the analysis, Quantofix® bias

6   decreased (-0.30 kg N m^{-3}), but continued being significantly different than 0.

7   MAE and RMSE were comparatively higher for Quantofix® (MAE=0.49 kg NH_4^+-N m$^-$

8   ^{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

9   kg NH_4^+-N m^{-3}) when all the samples were considered, although improved for

10   Quantofix® when samples with NH_4^+-N concentrations > 5 kg N m^{-3} were excluded

11   (MAE=0.43 kg NH_4^+-N m^{-3}, RMSE=0.56 kg NH_4^+-N m^{-3}). Thus, expected errors would

12   be smaller for $EC_{1:9}$ than for Quantofix®.

13   The modeling efficiency and the index of agreement were higher for $EC_{1:9}$ than for

14   Quantofix® for all the samples and when samples with NH_4^+-N > 5 kg N m^{-3} were

15   excluded from the analysis (Table 4). The $EC_{1:9}$ methodology is able to give values of

16   NH_4^+-N concentrations that are more in agreement with laboratory NH_4^+-N than

17   Quantofix®.

18   The better performance of $EC_{1:9}$ can also be observed in the distribution of the errors.

19   For $EC_{1:9}$, 42 % of samples presented errors that were between -0.25 and 0.25 kg NH_4^+-

20   N m^{-3} whilst for Quantofix® only 16% of the samples presented errors in the range -

21   0.25 to 0.25 kg NH_4^+-N m^{-3} (Fig. 4). It can also be observed in Figure 4 that the errors

22   for $EC_{1:9}$ were concentrated around 0 whereas errors for Quantofix® are displaced to

23   the left in relation to the bias of the method.

1   Average estimation errors (Fig. 4) obtained in the evaluation of the method are in the

2   range between 0.2 and 0.4 kg NH_4^+-N m^{-3}. For average PS ammonium-N concentration

3   of fattening farms (average NH_4^+-N = 3.77 kg N m^{-3}), the error would be less than 10%

4   and less than 5% in half of the cases. When the method is used to estimate NH_4^+-N

5   concentration of maternity farms (average NH_4^+-N = 2.48 kg N m^{-3}) average error

6   increases to 16%. The errors are considered reasonable in order to estimate target PS

7   rates adjusted to crop N needs.

8   Comparison of pen *vs*. portable EC-meters

9   The pen EC-meter was able to estimate NH_4^+-N concentrations with the same reliability

10   as the portable EC-meter (Fig. 5). Pen $EC_{1:9}$ was unbiased as MB did not differ from 0.

11   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

12   those obtained with a portable EC-meter (Table 4). Pen MEF (0.74) and d (0.93) were

13   high and similar to the values obtained for the portable EC-meter (Table 4). These

14   results permit the recommendation of pen EC meters to measure NH_4^+-N concentrations

15   of slurry dilutions of 1:9 in the field. Pen EC-meters are more robust than portable EC-

16   meters, are cheaper and are better accepted by farmers.

17   Use of alternatives to distilled water for the dilution

18   There was a significant linear relation between $EC_{1:9}$ and NH_4^+-N concentration for

19   each of the four different types of dilution water analyzed (Table 5). Moreover, for each

20   type of water, the estimated value of the intercept (a, Table 5) did not differ

21   significantly from the EC of that water (EC_w, Table 5). For that reason, we obtained the

22   adjusted values of $EC_{1:9}$ ($EC_{1:9}^{adj}$) by subtracting the EC of the water used in the dilution

23   (EC_w) from $EC_{1:9}$, as shown in Eq. 7.

24    $$EC_{1:9}^{adj} = EC_{1:9} - EC_w \qquad\qquad \text{[Eq. 7]}$$

1   Then the $EC_{1:9}^{adj}$ for all PS samples and types of dilution water (N=128) were compared

2   to NH_4^+-N concentrations. A significant linear relationship was observed between $EC_{1:9}^{adj}$

3   and NH_4^+-N concentrations, (R^2= 0.95; p>0.001). The estimated values of the intercept

4   (-0.009) did not differ from 0 and the estimated value of the slope (0.999) did nor differ

5   from 1 (Fig. 6), indicating that $EC_{1:9}^{adj}$ is an unbiased estimator of NH_4^+-N concentration.

6   This is confirmed by the mean bias (0.01 kg NH_4^+-N m^{-3}) that did not differ

7   significantly form zero. The MAE (0.19 kg NH_4^+-N m^{-3}) and RMSE (0.25 kg NH_4^+-N

8   m^{-3}) values for $EC_{1:9}^{adj}$ were smaller than those obtained in the $EC_{1:9}$ evaluation, although

9   it has to be considered that, in this case, the "variability" of the samples was lower as

10   only 32 PS samples were used versus 97 PS samples in the evaluation of the method.

11   The modeling efficiency (0.94) and the index agreement (0.98) were better than in the

12   evaluation of the method for the same reasons as those explained above. It is possible to

13   use the water available on a farm to prepare the dilution if the water has an EC lower

14   than 1.9 dS m^{-1}. In this case, it is necessary to subtract the EC of the water from the EC

15   measured in the 1:9 dilution to obtain the NH_4^+-N concentration of the slurry.

16 **Conclusions**

17   Electrical conductivity ($EC_{1:9}$) measurement of pig slurry (PS), after dilution 1 part pig

18   slurry and to 9 parts distilled water, has proved to be a simple, inexpensive, accurate,

19   and robust for measuring PS ammonium-N concentration, across a wide range (1.0 to

20   7.6 kg NH_4^+-N m^{-3}). The $EC_{1:9}$ was an unbiased estimator of NH_4^+-N concentrations of

21   PS with average estimation error given by the mean absolute error of 0.4 kg NH_4^+-N m^{-}

22   ^{3}. The use of alternative waters for dilution, with EC up to 1.9 dS m^{-1}, was shown to

1 allow the successful adaptation of the methodology, only, to measurement of the EC of

2 the water and subtraction of the reading from $EC_{1:9}$.

3 This methodology is considered a useful tool for adjusting slurry rates at the moment of

4 spreading increasing slurry N use efficiency and diminishing the risk for nitrate

5 leaching and greenhouse gases emission. Acceptance by pig farmers has been excellent,

6 and Extension Services in collaboration with farmers associations technicians has

7 started its implementation in the area.

8

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4   35 pp.

1   **Legend figures**

2   **Figure 1.** Relationship between Quantofix® and laboratory ammonium-N concentration

3   (***, p<0.001; n=97).

4   **Figure 2.** Ammonium concentration determined by Quantofix® of standard solutions of

5   ammonium-chloride in the range 4 to 8 kg NH_4-N m^{-3} using the customary amount of

6   reagent and a double amount.

7   **Figure 3.** Relationship between $EC_{1:9}$ (dS m^{-1}) and laboratory ammonium-N

8   concentration (kg N m^{-3}) (***, p<0.001; n=97).

9   **Figure 4.** Distribution of errors for $EC_{1:9}$ ($EC_{1:9}$ – laboratory NH_4^+-N concentration) and

10   Quantofix® (Quantofix® - laboratory NH_4^+-N concentration) methods.

11   **Figure 5.** Relationship between $EC_{1:9}$ values measured with portable and pen

12   conductimeters (***p<0.001, n=61).

13   **Figure 6.** Relationship between $EC_{1:9}^{adj}$ ($EC_{1:9}$ -EC_w, dS m^{-1}) adjusted by the EC of the

14   dilution water (EC_w): D (distilled water); I1 (irrigation water EC_w: 1.86 dS m^{-1}); I2

15   (irrigation water EC_w: 0.55 dS m^{-1}), and T (tap water EC_w: 0.84 dS m^{-1}) and laboratory

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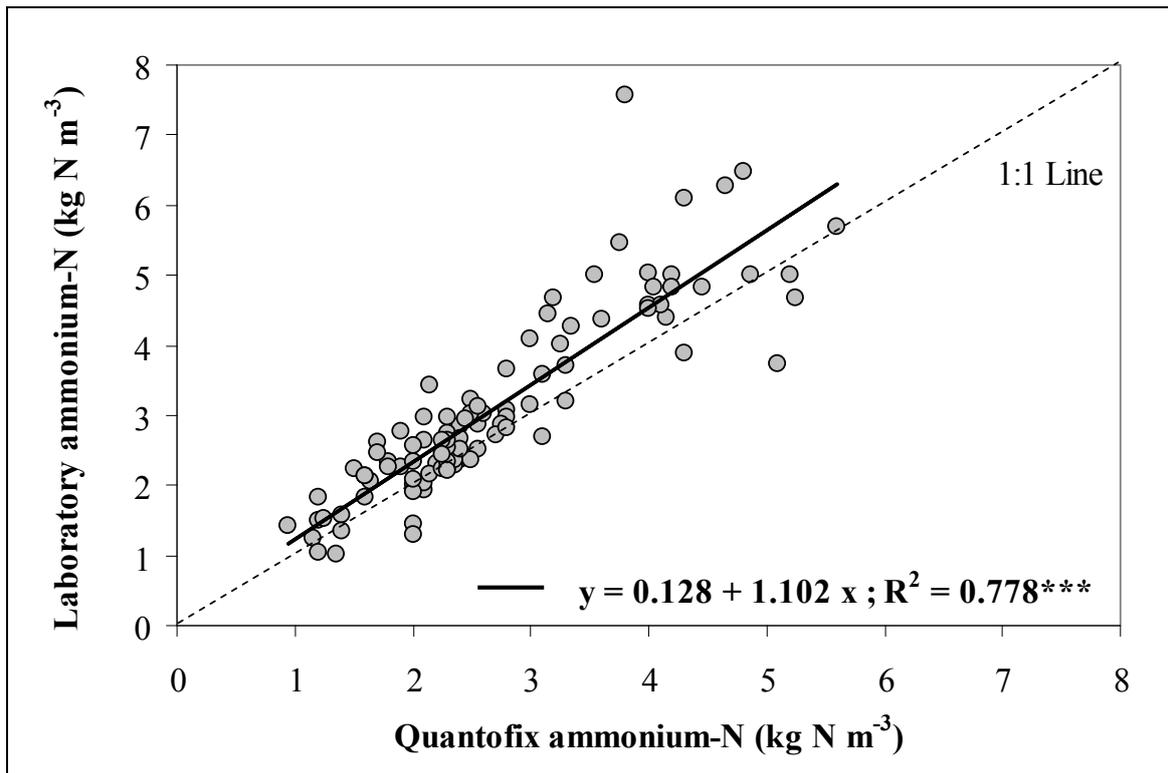
Fig. 1. Relationship between Quantofix® and laboratory ammonium-N concentration (***, p<0.001; n=97).
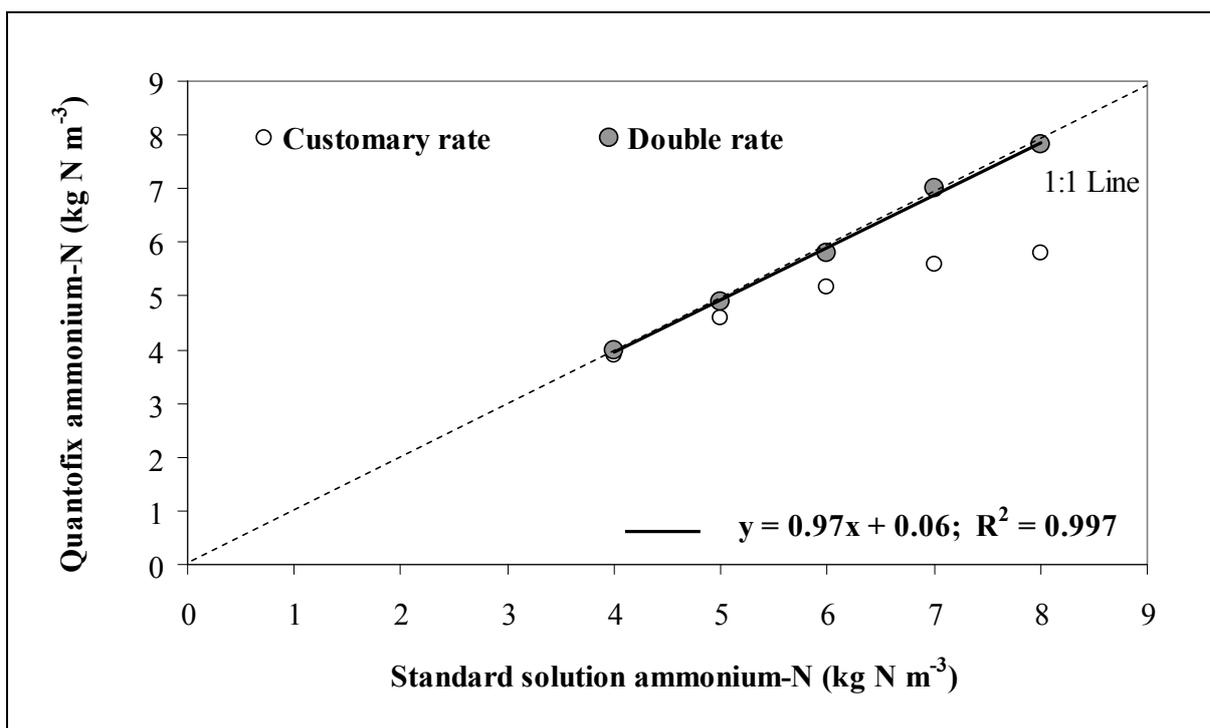
Fig. 2. Ammonium concentration determined by Quantofix® of standard solutions of ammonium-chloride in the range 4 to 8 kg NH_4^+-N m^{-3} using the customary amount of reagent and a double amount.
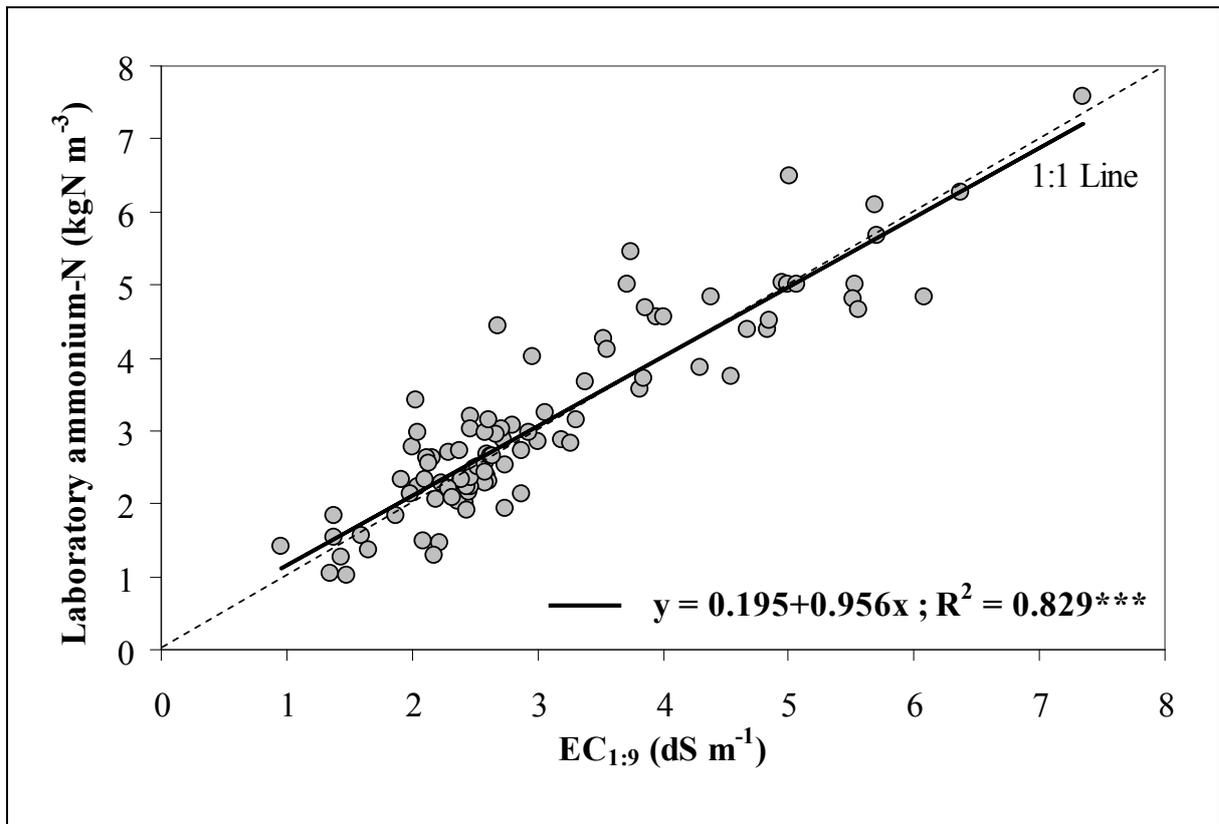
Fig. 3. Relationship between $EC_{1:9}$ (dS m^{-1}) and laboratory ammonium-N concentration (kg N m^{-3}) (***, $p<0.001$; n=97).
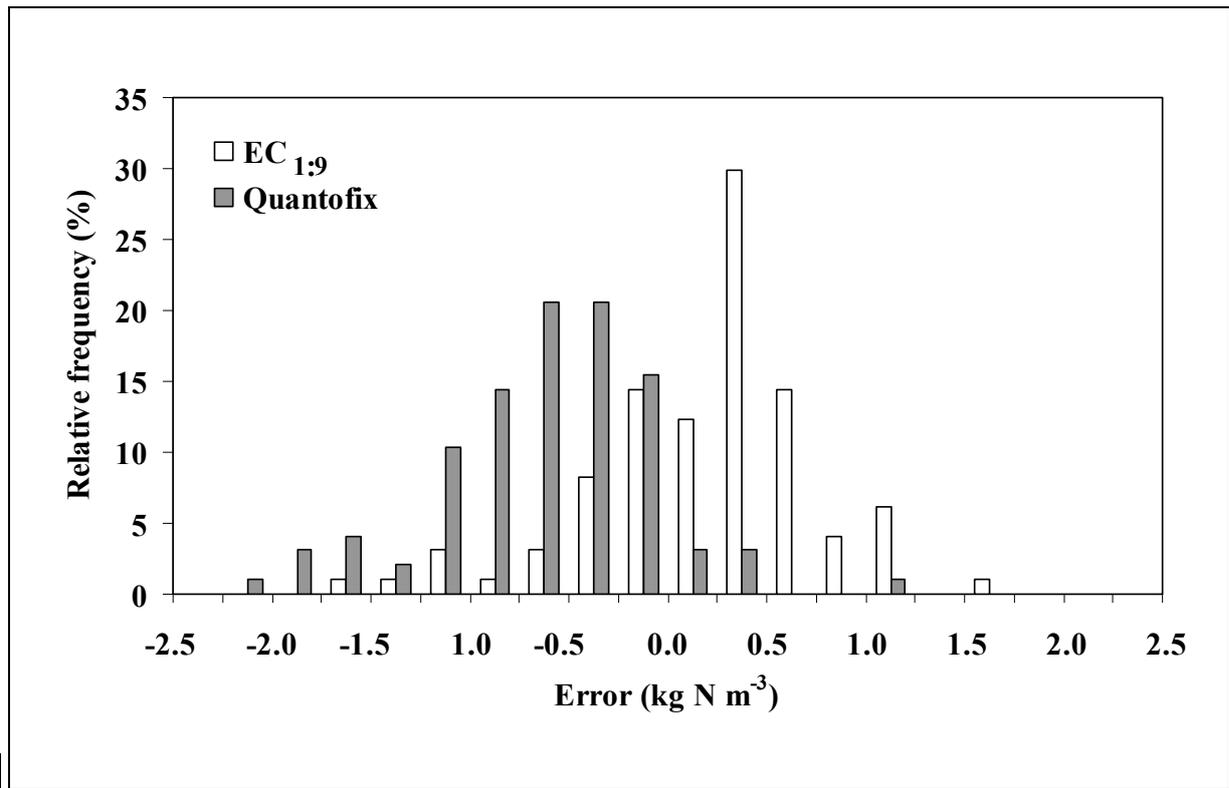
Fig. 4. Distribution of errors for $EC_{1:9}$ ($EC_{1:9}$ − laboratory NH_4^+-N concentration) and Quantofix® (Quantofix® - laboratory NH_4^+-N concentration) methods.
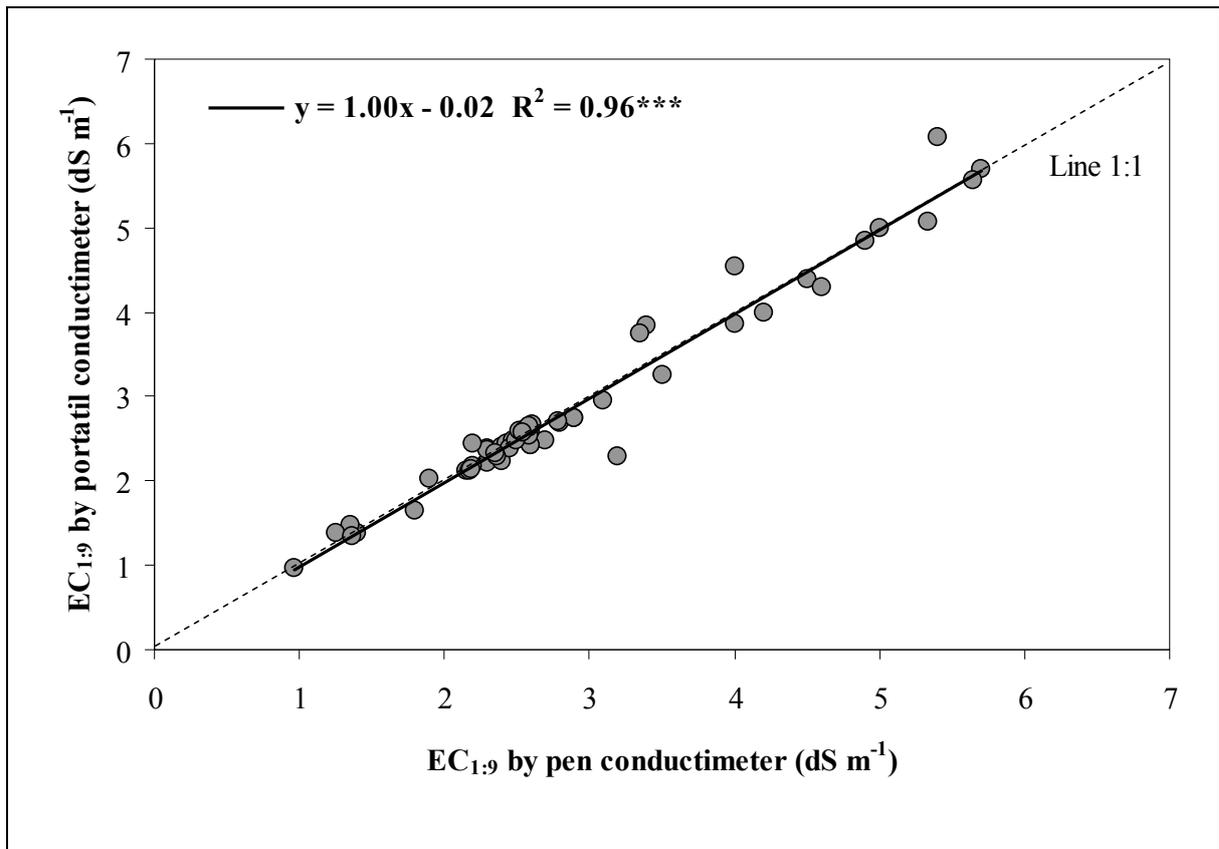
Fig. 5. Relationship between $EC_{1:9}$ values measured with portable and pen conductimeters (***$p<0.001$, n=61).
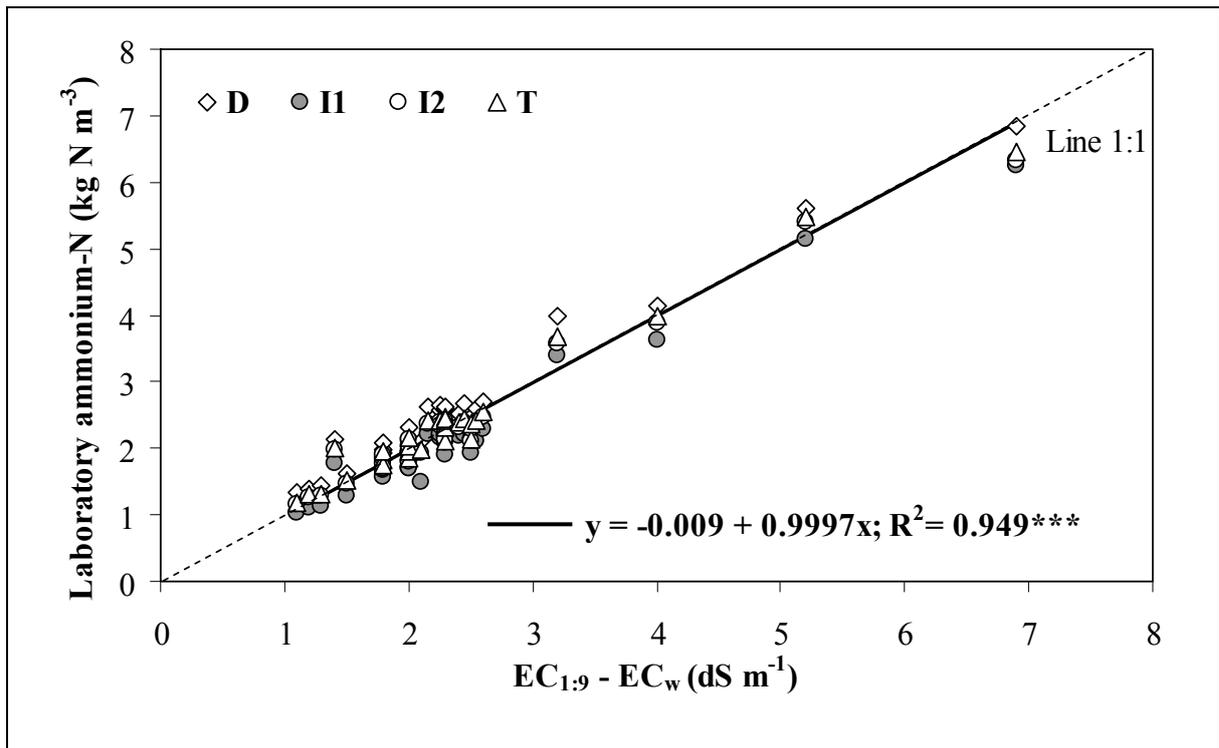
Fig. 6. Relationship between $EC_{1:9}^{adj}$ ($EC_{1:9}$ -EC_w, dS m^{-1}) adjusted by the EC of the dilution water (EC_w): D (distilled water); I1 (irrigation water EC_w: 1.86 dS m^{-1}); I2 (irrigation water EC_w: 0.55 dS m^{-1}), and T (tap water EC_w: 0.84 dS m^{-1}) and laboratory ammonium-N concentration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

|	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	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
NH_4^+-N /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 pig 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 nN=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: 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).

	Dn	$EC_{1.5}$	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
Dn	-	-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 ≤ 5 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 ($EC_{1:9}^{adj} = EC_{1:9} - EC_w$).

	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 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.

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***

*** $p < 0.001$.