

Development of a Farmer 'Friendly' Rapid Ammonium Nitrogen Test for Anaerobic Digestate

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Anaerobic Digestate Plant



Anaerobic Digestate Plant in Germany



Project Background

- Ammonia losses from anaerobic digestate – pollution source
- Reduces the Nitrogen value of the material
- Lab analysis of total nitrogen will not represent the actual value of ammonium nitrogen if losses have occurred
- Storage conditions and storage length are essential to minimise nitrogen losses

Project Objective

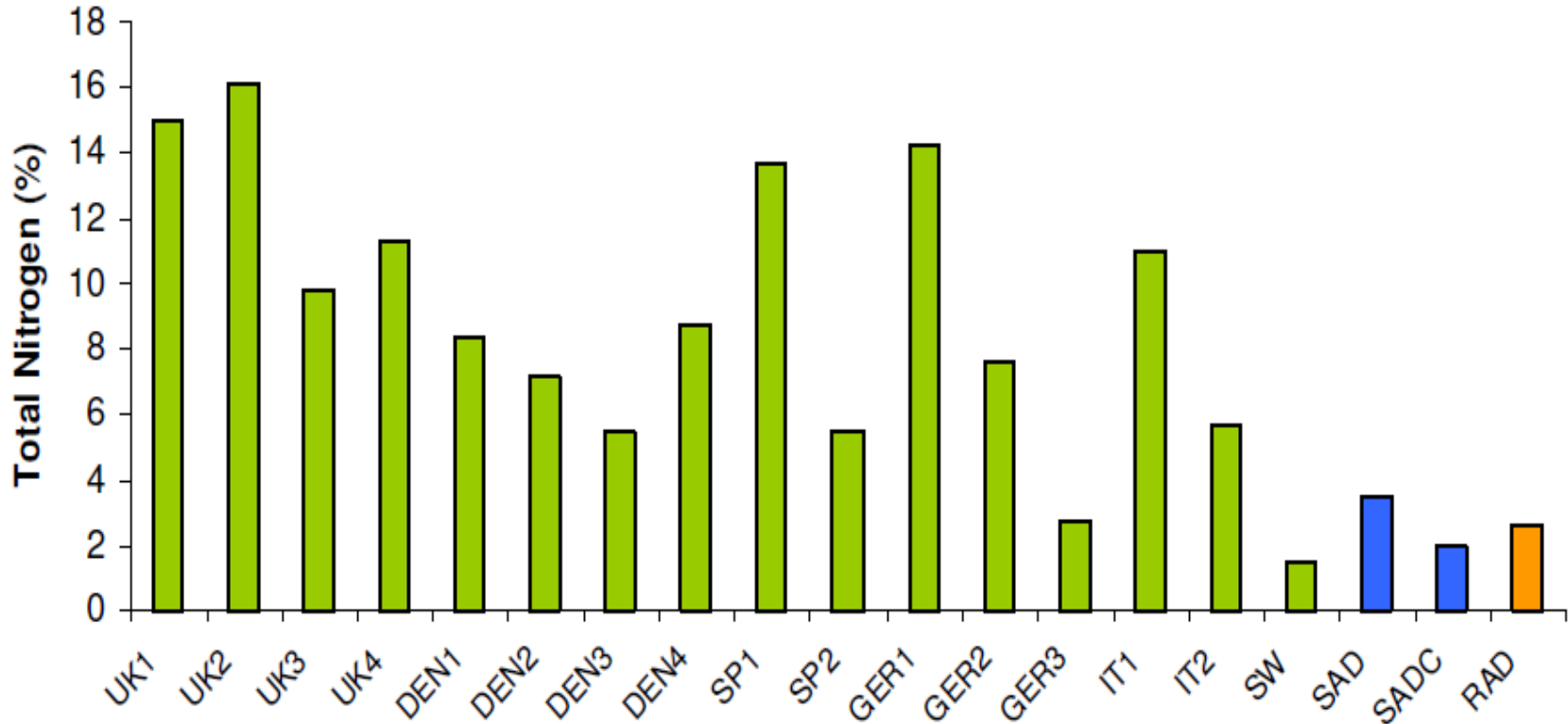
'To develop a simple and farmer friendly rapid Ammonium test for use with Anaerobic Digestates '

List of Anaerobic Digestate materials, feedstocks and sources*

Code	Country of Origin	Feedstock Material Details	Source
UK1	UK	Not Reported	Rigby & Smith, 2011
UK2	UK	Not Reported	Rigby & Smith, 2011
UK3	UK	Not Reported	Rigby & Smith, 2011
UK4	UK	Dairy Manure, Blood, Food waste, Chicken Manure	SAC, 2007
DEN1	Denmark	Not Reported	SAC, 2007
DEN2	Denmark	Dairy Manure, Pig Manure, Poultry Abattoir Waste	SAC, 2007
DEN3	Denmark	Cattle Slurry	SAC, 2007
DEN4	Denmark	Pig Slurry	SAC, 2007
SP1	Spain	Pig and Dairy Slurry	Alburquerque <i>et al.</i> 2012
SP2	Spain	Cattle Slurry	Alburquerque <i>et al.</i> 2012
GER1	Germany	Food Waste	AD Centre, 2009
GER2	Germany	Energy Crops	AD Centre, 2009
GER3	Germany	Multiple sources	Blom <i>et al.</i> 2009
IT1	Italy	Waste Water Sludge	Tambone <i>et al.</i> 2010
IT2	Italy	Composted Waste Water Sludge	Tambone <i>et al.</i> 2010
SW	Switzerland	Animal Manures and Biowaste	Fuchs <i>et al.</i> 2007
SAD	Germany	Food/Manure	
SADC	Germany	Food/Manure	
RAD	England	Food/Manure	

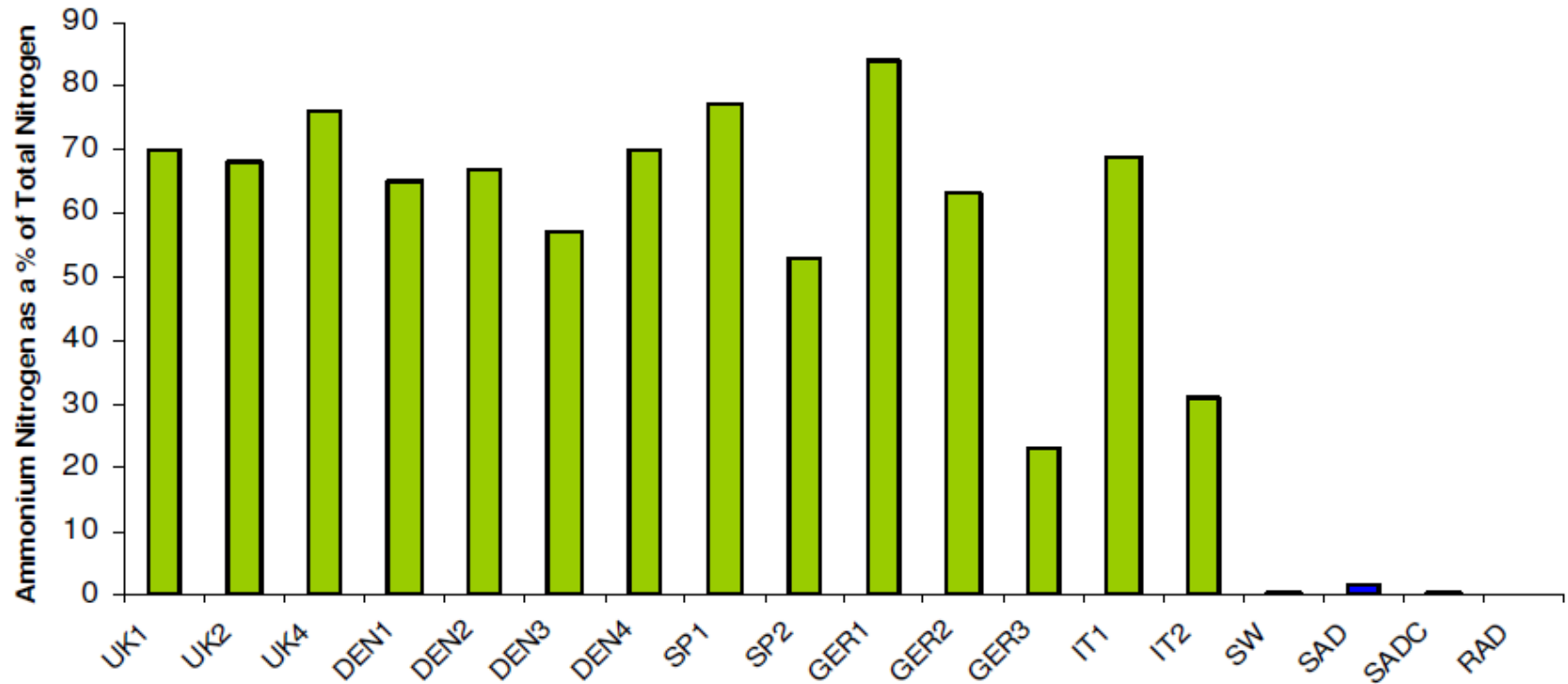
*Prasad, M., Lee, A., & Gaffney, M.T. (2013). A detailed chemical and nutrient characterisation of compost and AD fibre. <http://www.rx3.ie/MDGUploadedFiles/file/rx3%20MDR0598%20Rp0021%20Munoo%20May%202013%20F03.pdf>

Total Nitrogen content of anaerobic digestates from selected EU countries



Prasad, M., Lee, A., & Gaffney, M.T. (2013). A detailed chemical and nutrient characterisation of compost and AD fibre. <http://www.rx3.ie/MDGUploadedFiles/file/rx3%20MDR0598%20Rp0021%20Munoo%20May%202013%20F03.pdf>

Ammonium Nitrogen expressed as a percentage of Total Nitrogen

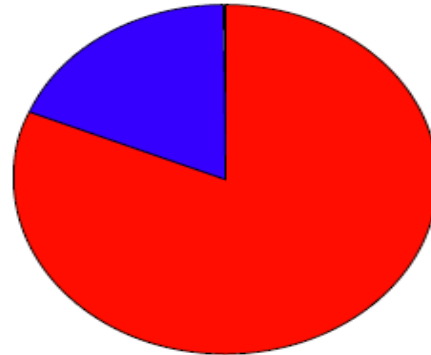


Prasad, M., Lee, A., & Gaffney, M.T. (2013). A detailed chemical and nutrient characterisation of compost and AD fibre. <http://www.rx3.ie/MDGUploadedFiles/file/rx3%20MDR0598%20Rp0021%20Munoo%20May%202013%20F03.pdf>

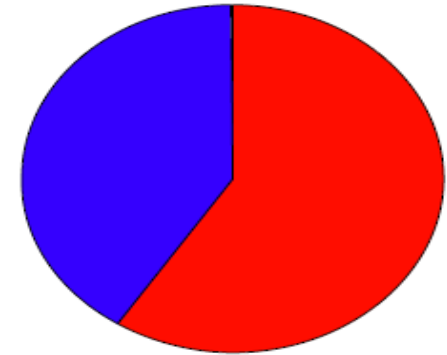
Readily available (ammonium) nitrogen – RAN

Food-based digestate

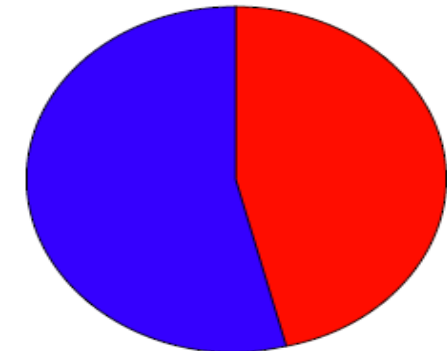
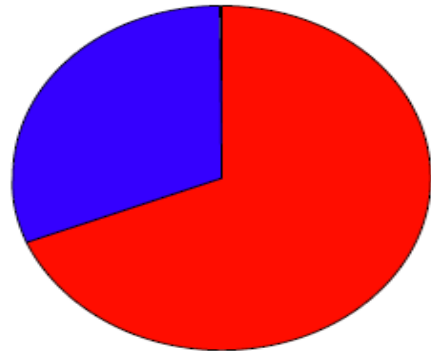
Manure-based digestate



Pig slurry



Cattle slurry



Anaerobic Digestate Storage

- Digestate is produced and stored throughout the year
- Only applied during the growing season
- Length of storage period depends on geographical area, soil type, winter rainfall, natural vegetation etc
- Temperate climate normal storage 6 to 9 months
- In some countries set period of storage of digestate is compulsory

European regulations concerning storage and application of anaerobic digestate

Country	Maximum nutrient load	Required storage capacity	Compulsory season for spreading
Austria	170 kg N/ha/yr	6 months	28 Feb - 5 Oct
Denmark	170 kg N/ha/yr (cattle) 140 kg N/kg/yr (pig)	9 months	1 Feb - harvest
Italy	170 - 500 kg N/ha/yr	90 - 180 days	1 Feb - 1 Dec
Sweden	170kg N/ha/yr (calculated from livestock units per ha)	6 - 10 months	1 Feb - 1 Dec
Northern Ireland	170 kg N/ha/yr	4 months	1 Feb - 14 Oct
Germany	170 kg N/ha/yr	6 months	1 Feb - 31 Oct Arable land 1 Feb - 14 Nov Grassland

Anaerobic Digestate Storage

- To avoid ammonia and methane emission measures have to taken
- For example digestate storage types
 - Storage tank with a tight membrane
 - Flexible Storage bags
 - Floating layer e.g. thin layer of plastic pieces, clay pebbles or chopped straw
- In some countries there are financial incentives to establish covered digestate store (Denmark)

Two methods of digestate storage



Bag storage tank

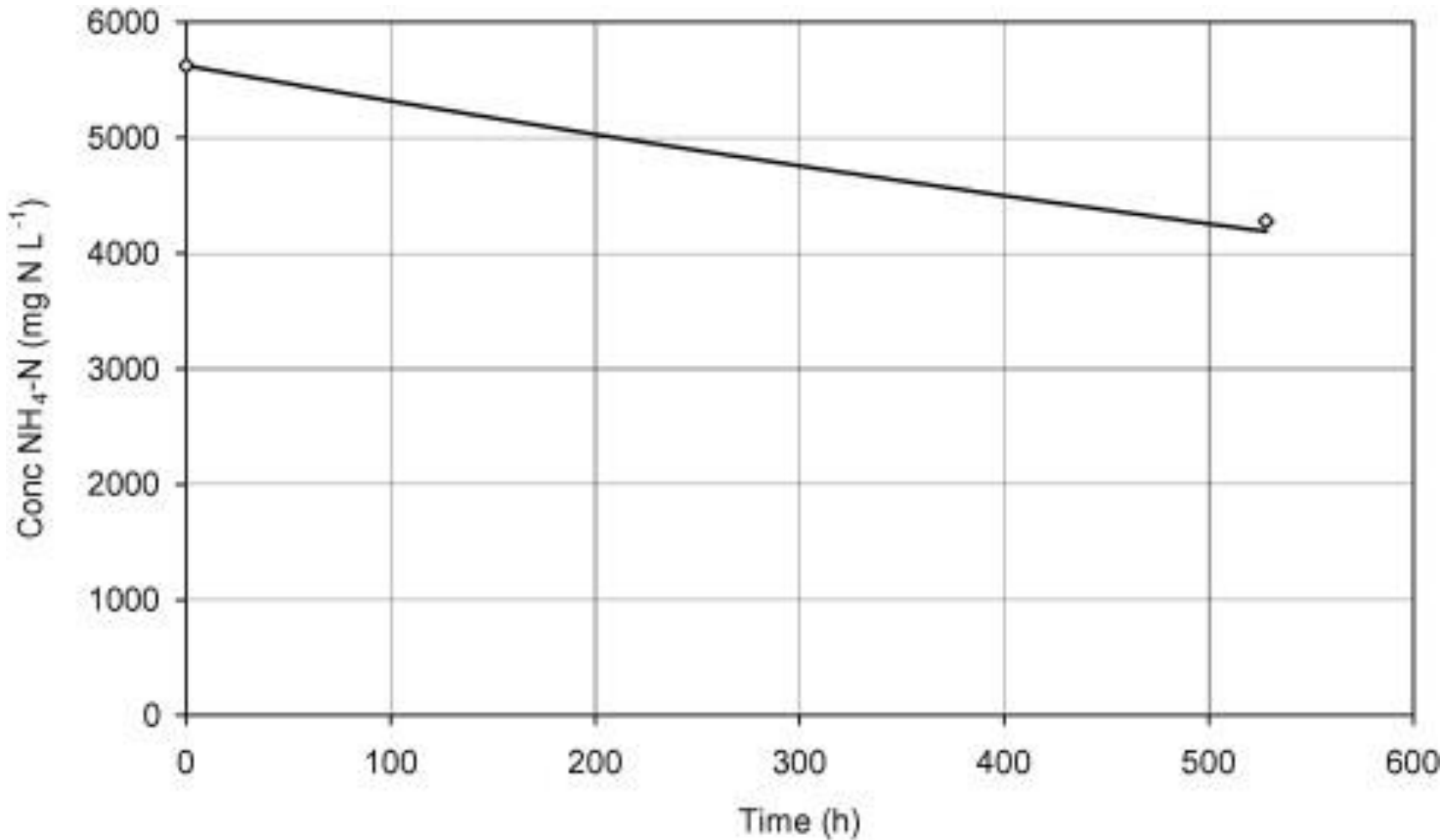


Digestate storage tank with tent cover

Floating layer storage

- This layer can be natural
- Crust of at least 10–20cm, a floating layer of plastic pieces, clay pebbles or chopped straw, etc.
- Please note however, that chopped straw can give off methane when decomposing

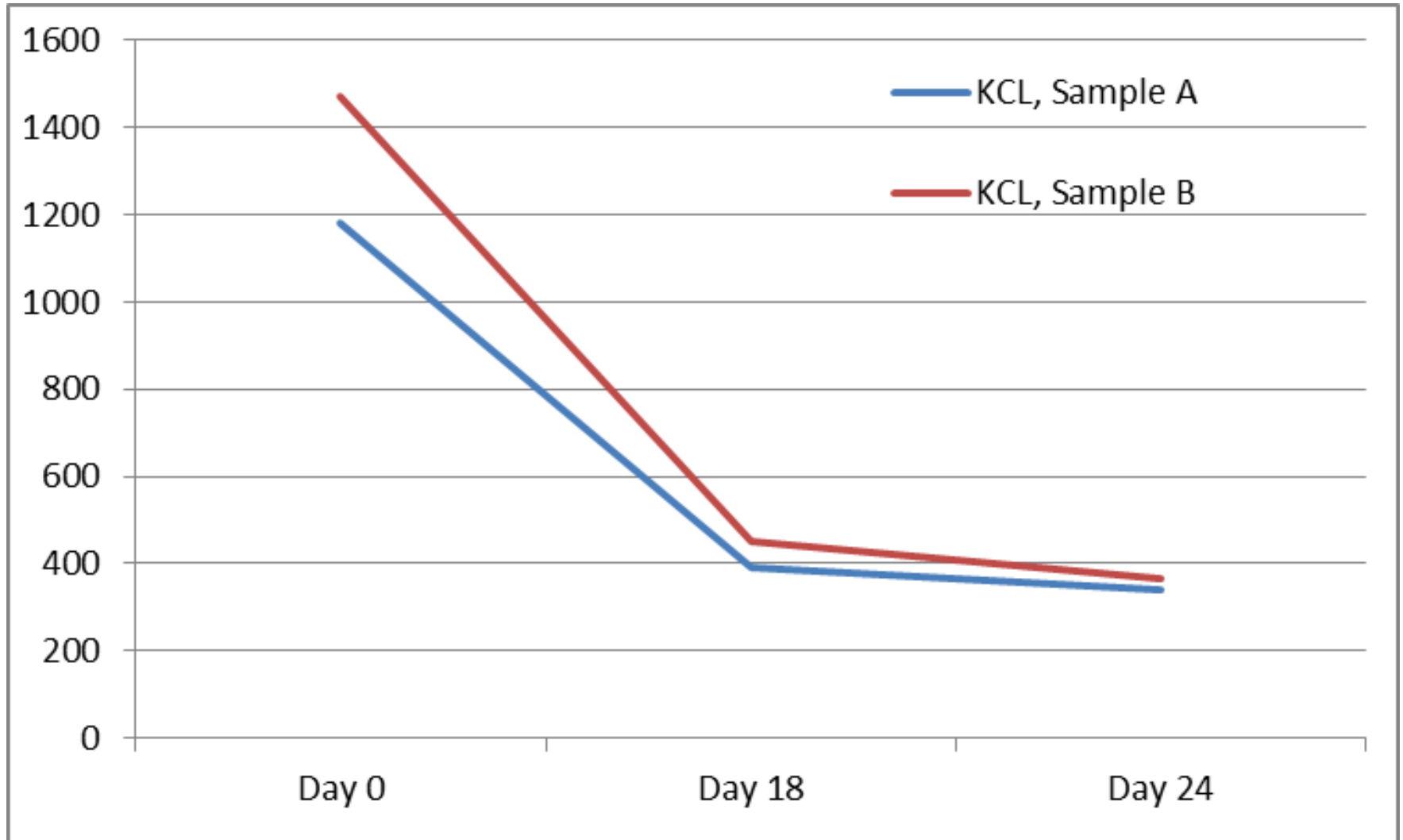
Graphical representation of ammonia losses over time



Whelan, M.J., Everitt, & Villa, R. (2010) A mass transfer model of ammonia volatilisation from anaerobic digestate. *Waste Management*. 30.10 p1808-1812

Loss of $\text{NH}_4\text{-N}$ from digestate to atmosphere over 24 days

(Development of a Rapid and Simple Test for Ammonium-N Determination in Digestate. Report to DOECLG)



Feedstock and Origin of Anaerobic Digestates*

Digestate Sample	Feedstock (Origin)
A	Food waste (Ireland)
B	Manure, dairy sludge, sludge and grease sludge (Ireland)
C	Manure, grass and sewage sludge (Northern Ireland)
D	Manure and small amount of sewage sludge (Ireland)
E	Manure and grease (Ireland)

Three of the samples had sufficient solids to supply enough fibre for analysis. For these, digestate was passed through a 1 mm sieve to extract the fibre

* Prasad, M., Murphy, S., Lee, A., Burgess, K. & Gaffney, M.T. (2014) Development of a Rapid and Simple Test for Ammonium-N Determination in Digestate. Report to DOECLG (Final Project Report Submitted)

Methods of Analysis

- 1) Total Kjeldahl N (TKN)
- 2) KCl Extractable NH₄-N by Auto Analyzer (Lachat FIA)
- 3) KCl Extractable NH₄-N by rapid Quantofix ammonium strip read using a digital readout reflectometer (Nagel)
- 4) KCl Extractable NH₄-N by rapid Quantofix ammonium strip read visually (on a limited number of samples)
- 5) Other characterisation methods were also conducted such as pH, Dry Matter and Electrical Conductivity

Methodology

- 1) 250 ml of digestate was extracted using 0.5M Potassium Chloride (18.5 grams in 250 ml)
- 2) It is important to take representative sample (homogenised by shaking or mixing by glass rod)
- 3) Sample shaken continuously for 30 minutes
- 4) Sample filtered using filter paper (Whatman No.1 240)
- 5) Quantofix Ammonium strip was used to determine Ammonium nitrogen
- 6) If reading was much above the desired range diluted and resampled
- 7) Samples were also immediately analysed for ammonium N using an Auto Analyzer (Lachat FIA)

Procedure for the Rapid test for Ammonium

Digestate, liquor and fibre



Shaking sample with KCL extractant



Filtering the sample

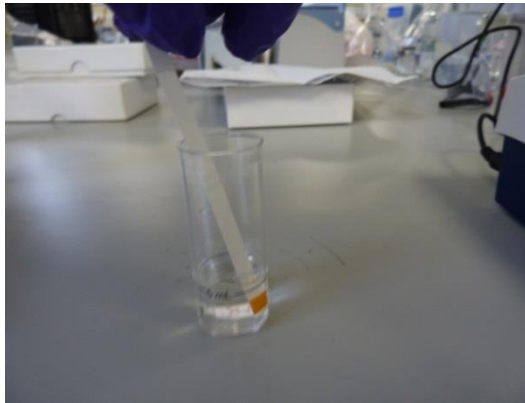


On Site Filtering

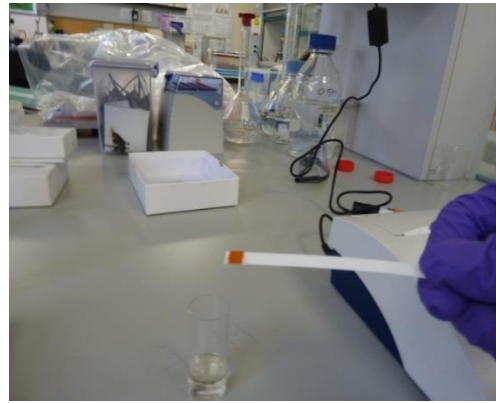


Procedure for examining the Ammonium strips visually and using the reflectometer

Add reagents to plastic cylinder and insert strip for five seconds



Remove and allow colour to develop



Match the colour to the chart to deduce the concentration (visual method)



Insert in to reflectometer for digital measurement



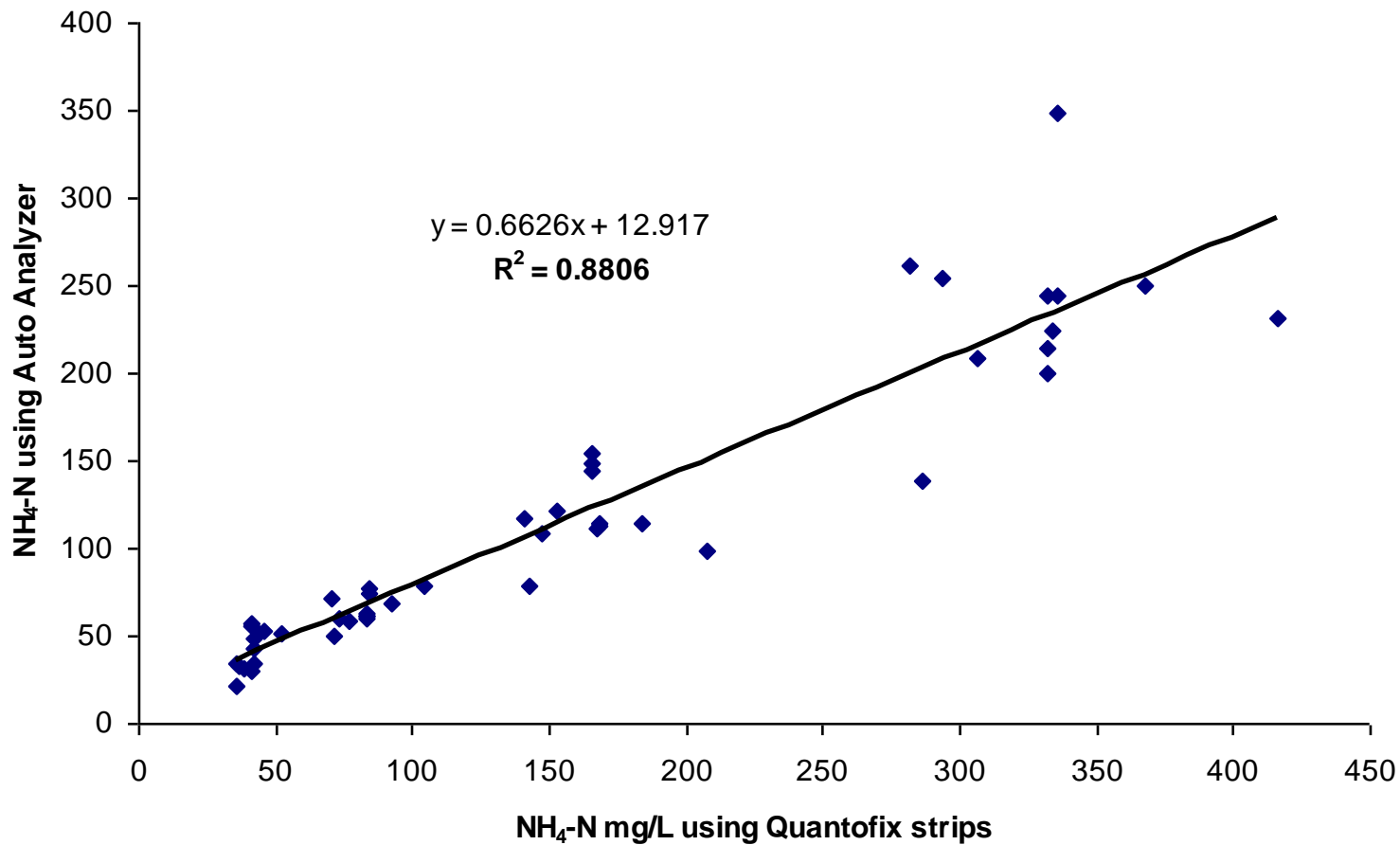
Samples were also run on an auto analyser to compare results



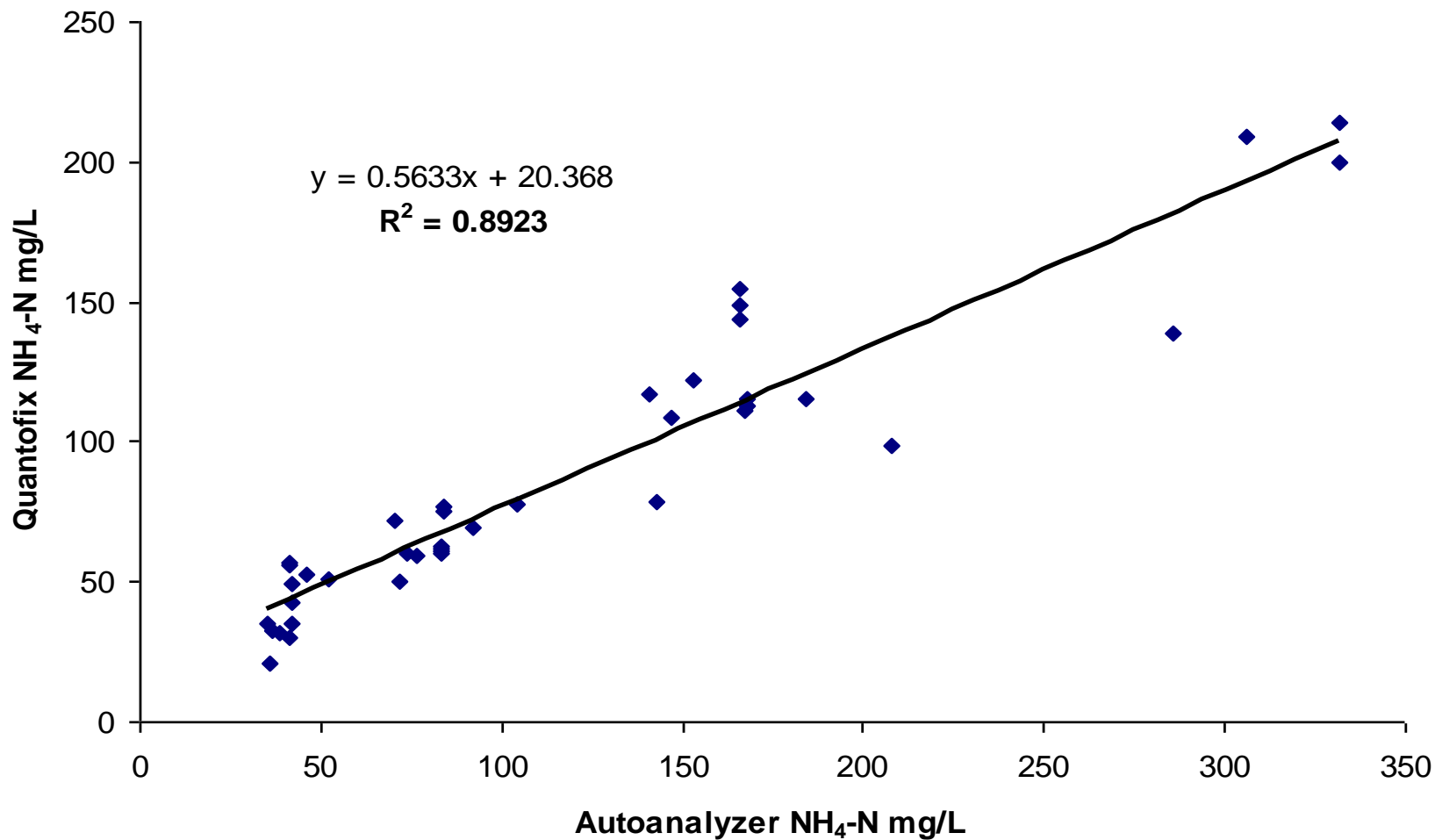
Total Nitrogen & Ammonium-N: Samples used in study

Sample	Total N % DM	% NH₄ - N/TN
A	6.47	56%
B	4.82	66%
C	2.74	46%
D	3.28	48%

Relationship between Quantofix strip $\text{NH}_4\text{-N}$ and Auto Analyser $\text{NH}_4\text{-N}$ (All Dilutions)

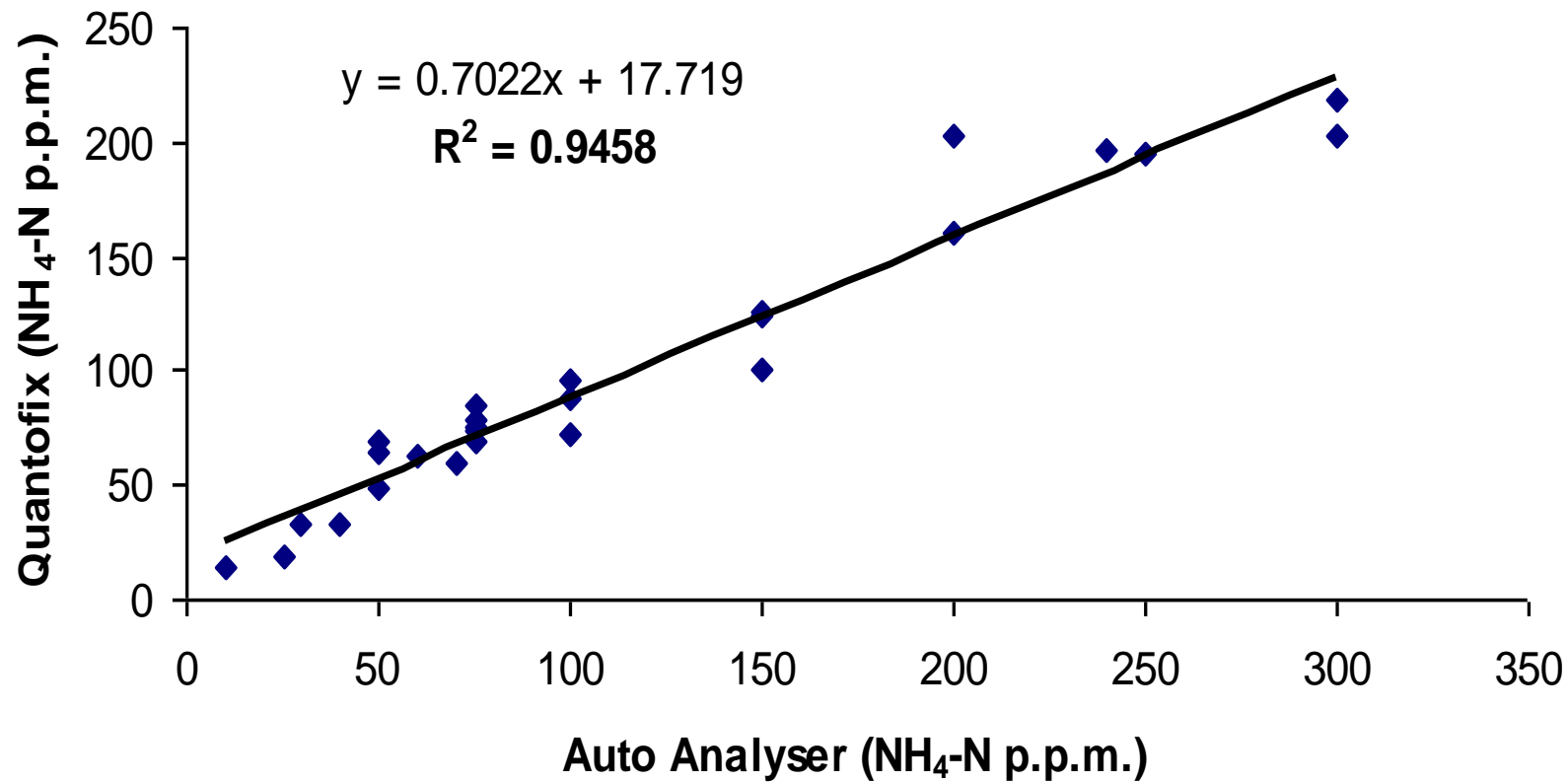


Relationship between Auto Analyser NH₄-N and
Quantofix reflectometer NH₄-N
(<215mg/L : All Dilutions)



Comparison between NH₄-N by Auto Analyser and
Quantofix NH₄-N strips

(Sampled at Days 0,6 &12; Dilution 1:4)



Relationship between Merck Ammonium Strip and standard lab method on slurry samples

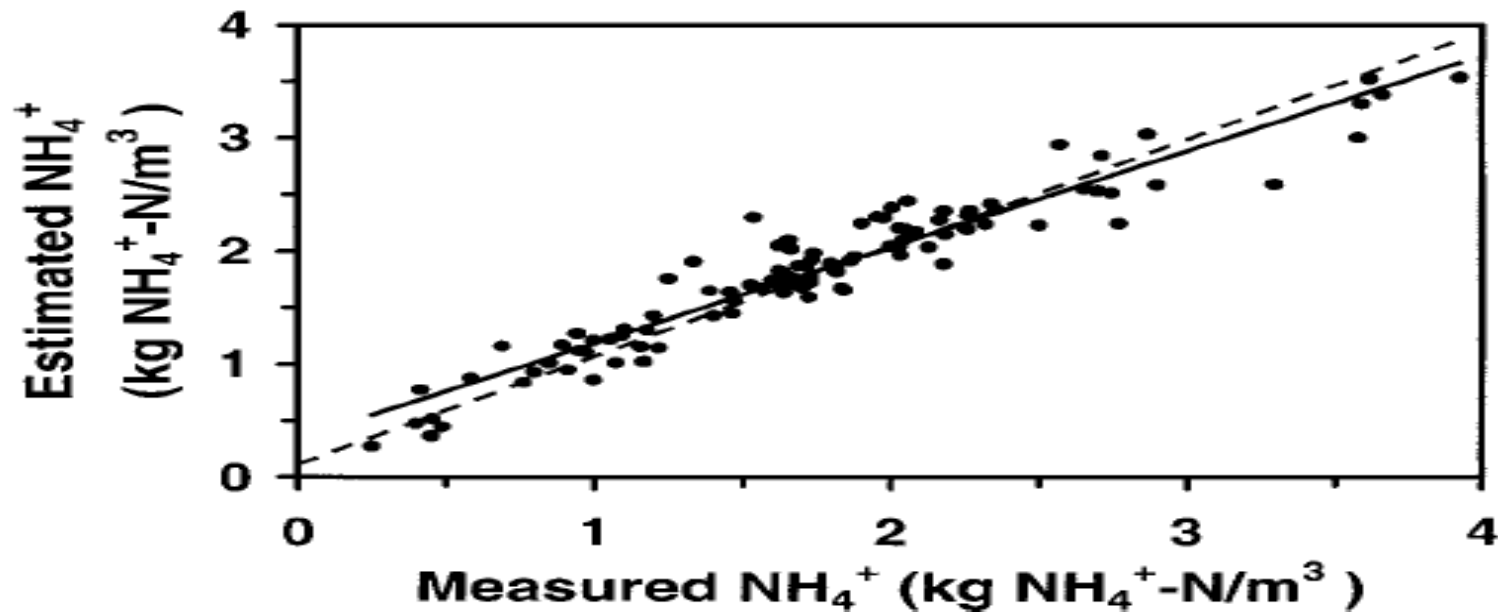
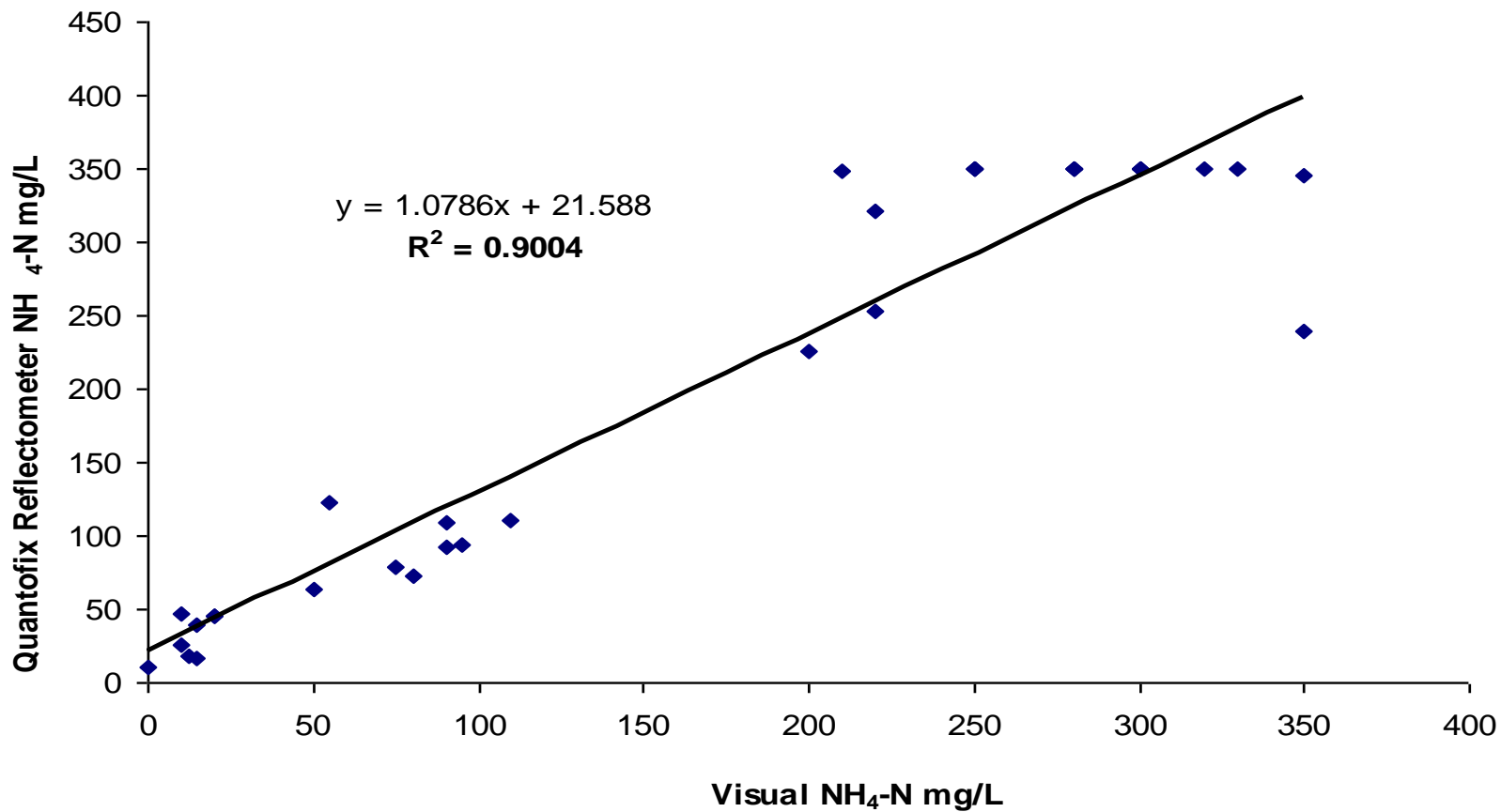


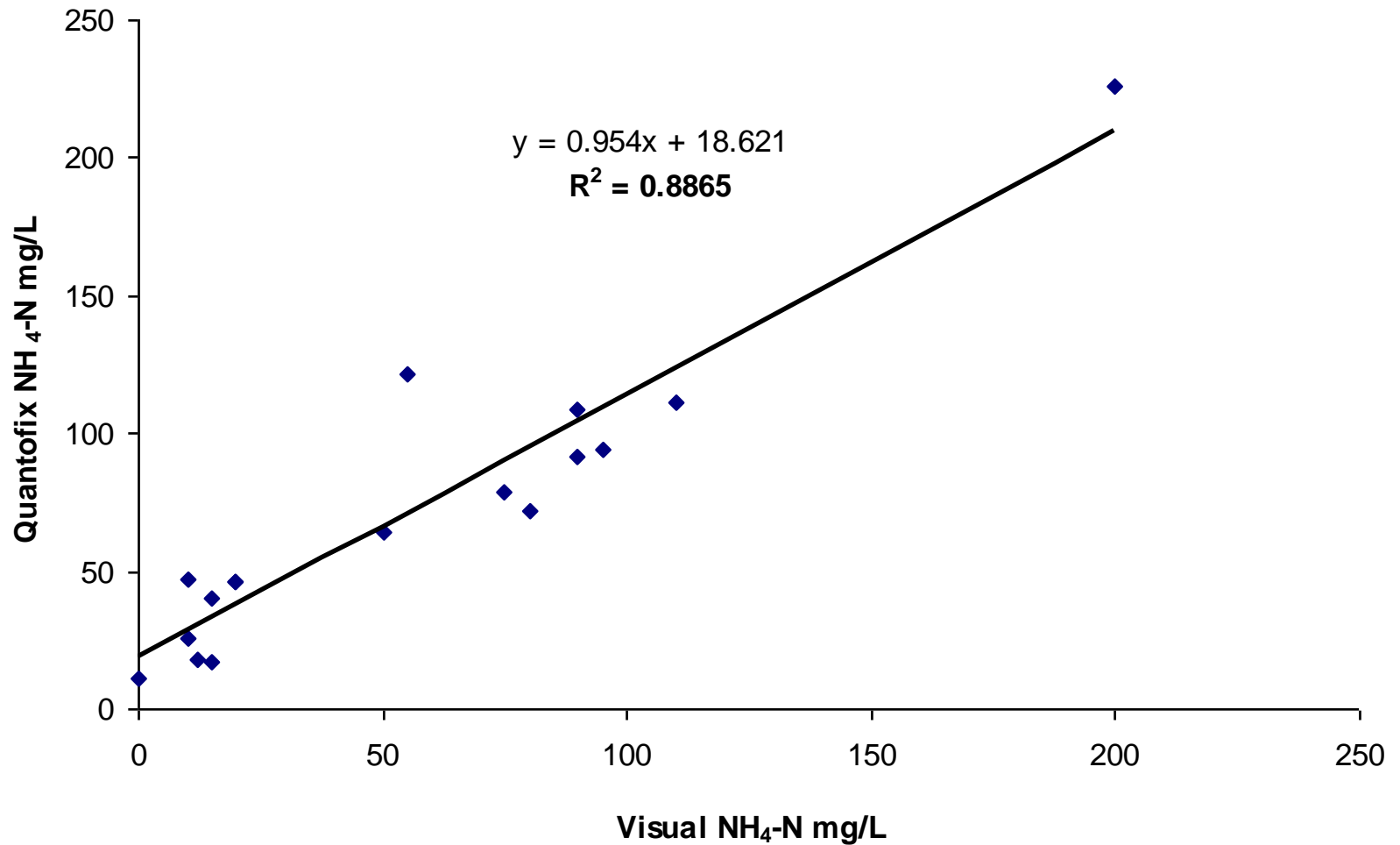
Figure 4. Ammonium N concentrations in dairy manure samples estimated with the reflectometer versus standard laboratory methods (n = 104). The dashed line represents a line with slope = 1 and intercept = 0. The solid line represents the regression equation ($\hat{y} = 0.34 + 0.84x$).

Van Kessel, J.S., Reeves, J.B. & Thompson, R.B. (1999) Rapid on-farm analysis of manure nutrients using quick tests. *J. Prod. Agric.* 12.2 p215-224

Relationship between Visual NH₄-N and NH₄-N by Quantofix Reflectometer



Relationship between visual NH₄-N and Quantofix reflectometer NH₄-N
(<200 mg/L)



Conclusion

- The rapid N test based on the Ammonium Strip and the reflectometer gave satisfactory results. (Trend to underestimate values at higher concentrations)
- Visual assessment of strips was satisfactory but not optimum. Greater experience would be needed for this approach
- Dilution of samples critical (1: 4 usually sufficient)
- Data indicates optimal measurement of ammonium N at <200 mg/L
- A small amount of training may be required (1/2 Day)
- The cost of the reflectometer (€500 approx) maybe problematic but this could be pooled by AD operators, haulers and by farmers
- The cost of the analysis is low, less than €2 per sample and with repeated use more likely <€1

Acknowledgments

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- (C) Teagasc Walsh Fellowship Scheme (*S. Murphy, A. Lee*)

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