Development of a rapid and simple test for ammonium-N determination in anaerobic digestion

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Abstract
Ammonia losses is taking place during the storage of anaerobic digestion (AD) slurry for several months, before applied as crop fertilizer. Ammonia has a high propensity to volatise particularly at high pH and due to higher NH_3:NH_4 ratio and this leads to reduction of the nitrogen fertilizing value, which is of farmers ignorance. The scope of the present study was to develop a rapid ammonium quantification method for AD digestate which could be used to determine ammonium N in digestate in order to reliably identify how much NH_4-N is actually present after storage and is available for plant uptake. Five sources of AD digestate were obtained from Ireland, and were characterized (pH, EC, dry matter, total Kjeldahl nitrogen, extractable NH_4-N etc.). Digestate were stored in 25 L containers that were left open to atmosphere (Irish summer, 2013) to allow nitrogen to deplete. The results showed clearly that considerable amounts of nitrogen are lost from digestate in storage open to the atmosphere. Given the transient nature of NH_4-N in these materials, the need for this analysis of simple rapid testing methods to reliably determine the quantity of inorganic nitrogen (ammonium N) at the time of application to land is very important. The results also showed that it is possible to use NH_4-N detection strips with the Quantofix reflectometer to determine accurately the NH_4-N in whole digestate, digestate fibre and digestate liquor. The use of the reflectometer with automated digital readout gives more accurate results but needed dilution, and it is likely to avoid the bias (and need for extra training) that can occur when readings are done visually. Nevertheless we found the visual method still gives satisfactory results.

Keywords: ammonium release; rapid detection; anaerobic digestion; nitrogen uptake; digestate; ammonia volatization; ammonium strips; Quantofix

Introduction
The popularity of the biogas process has grown since the 1970s amidst rises in energy prices and worries about the detrimental impact of fossil such as slurry fuels on global warming. The anaerobic digestion (AD) process successfully convert biomass e.g. slurry and discarded food into to economically products energy source and a digestate that is a potential fertilizer and soil amendment. In most part of Europe the animal farms must store the digestate slurry in specially designed tanks with a total capacity to 6 to 9 months slurry production. Storage of AD slurry is rising due to restriction of the application period as crop fertilizer to only 4-6 months in interval close to or during the growing season. Not all the storage tanks have membrane covers to reduce ammonia losses much of the nitrogen in the digestate is in an ammonical form that is ammonium NH_4 and ammonia NH_3 (together over 80%) and which is available for plant uptake. However ammonia has a high propensity to volatise particularly at high pH and due to higher NH_3:NH_4 ratio. This leads to reduction of the nitrogen fertilizing value. The residual nitrogen after ammonia is lost and is bound in the organic matter and will behave in a manner similar to compost N, that is, it will have very low nitrogen release rate (Fuchs et al., 2007; Prasad et al., 2013).
The objective of this investigation was to develop a rapid ammonium quantification method for AD digestate which could be used to determine ammonium N in digestate in order to reliably identify how much NH_4-N is actually present after storage, rather than dependence upon the results of a laboratory analysis which may have been carried out prior to storage and not reflect the likely nitrogen release rates and plant uptake levels.

Materials and Methods
For the current study, five sources of AD digestate were obtained, four from Ireland and one from Northern Ireland. The whole digestates (liquid and fibre fraction, if present) from the five sources were characterized (pH, EC, dry matter, total Kjeldahl nitrogen etc). They were stored in 25 L containers that were left open to atmosphere (Irish summer, 2013) to allow nitrogen to deplete, giving a range of levels. Samples were taken regularly to allow for a wide range of NH_4-N to subject to analysis. These samples were analysed immediately or were stored in cold room in sealed containers.
Samples taken were analysed for:

- Total Kjeldahl N (TKN) by Auto Analyzer
- KCl Extractable NH_4-N by Auto Analyzer
- KCl Extractable NH_4-N by rapid Quantofix ammonium strip read using a digital readout reflectometer (Nagel) and using a visual assessment of colour

Results

The relationship between the lab flow injection AA method was good up to 180 mg/L and at higher concertation the relationship deteriorated (Fig. 1). The relationship between the digital Quantofix and the visual method was also good up to 200 mg/L but the Quantofix was not able to read above 200 mg/L.

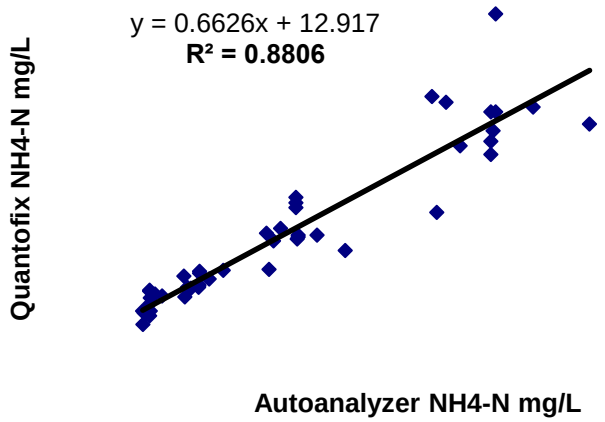

Figure 1. Relationship in determination of NH_4-N between Quantofix strip and FIA Autoanalyser.

We investigated ammonia volatilization from samples from 2 separate sites in Ireland (A) and (B) by measuring KCl extractable NH_4-N on samples. Ammonia loses were substantial especially at the start (Table 1) and it was found losses of around 70% over 24 days.

Table 1. Loss of NH_4-N from digestate to atmosphere over 24 days. Values are in mg NH_4-N/L retained in digest.

	Day 0	**Day 18**	**Day 24**
KCL, Sample 1	1180	393.2	338.0
KCL, Sample 2	1472	452.8	366.4

Conclusion

The results show clearly that considerable amounts of nitrogen are lost from digestate in storage open to the atmosphere. These results are in agreement by other workers. Given the transient nature of NH_4-N in these materials, the need for this analysis of simple rapid testing methods to reliably determine the quantity of inorganic nitrogen (ammonium N) at the time of application to land is very important. The results also showed clearly that it is possible to use NH_4-N detection strips with the Quantofix reflectometer to determine accurately the NH_4-N in whole digestate, digestate fibre and digestate liquor. The use of the reflectometer with automated digital readout gives more accurate results but needed dilution, and it is likely to avoid the bias (and need for extra training) that can occur when readings are done visually.