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# Nitrous oxide emissions and nitrogen use efficiency of manure and digestates applied to spring barley



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#### ABSTRACT

Digestates produced by anaerobic treatment of manure and organic wastes for biogas production are rich in nutrients which should be recycled to agricultural land to sustain crop growth. However, digestate properties are highly variable, complicating the prediction of agronomic value and environmental impact. The objective of this study was to assess nitrous oxide (N2O) emissions and nitrogen use efficiency during growth of spring barley (Hordeum vulgare L.) when fertilized with digestates and untreated manure, and to relate emission patterns to properties of soil and manure materials. Experimental treatments received 100 kg  $NH_4^+$ -N ha<sup>-1</sup> in either pig slurry (PS), cattle slurry (CS), a slurrybased digestate from Maabjerg Bioenergy (MBD), or cattle slurry mixed with digested and dewatered sewage sludge (CS+DDS). Ammonium sulfate (MIN) and unfertilized soil (Ctrl) served as references. Cumulative N<sub>2</sub>O-N emissions at harvest ranged from 0.02 to  $1.97 \text{ kg ha}^{-1}$ , and net emissions corresponded to 0.10–0.41% of total N input. According to a graphical model  $N_2O$  emissions were related to soil NO<sub>3</sub><sup>-</sup>, rather than NH<sub>4</sub><sup>+</sup> availability, indicating that denitrification was the main source of N<sub>2</sub>O. When observations were fitted to an empirical model of cumulated N<sub>2</sub>O emissions, nitrification in manure hotspots was identified as a main driver of N<sub>2</sub>O emissions, but low soil NO<sub>3</sub><sup>-</sup> availability suggested that the role of nitrification was indirect, via coupled nitrification-denitrification. Yield-scaled emissions ranged from 0.04 to 0.39 g  $N_2$ O-N kg<sup>-1</sup> grain yield. The emissions intensity of MBD was lower than that of untreated manure, and similar to mineral fertilizer. In contrast, treatment CS+DDS containing also digested organic material had the highest total and yield-scaled N<sub>2</sub>O emissions. Thus, agronomic and environmental performance of digestates can not be predicted from management, but must take specific soil and manure properties into account.

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#### 1. Introduction

Heat and power generation from anaerobic digestion may substitute fossil fuels and thereby reduce radiative forcing from anthropogenic emissions of carbon dioxide (CO<sub>2</sub>) (Don et al., 2012). In accordance with an energy policy decision to become independent from fossil fuels by 2050 (Danish Climate and Energy Policy, 2013), the capacity and number of biogas plants in Denmark is increasing to fulfil an ambition to process 50% of livestock manure in biogas plants (Thygesen et al., 2014). This development is promoted by economic incentives to ensure profitability in biogas production; for farmers there is typically no cost associated with the transport and processing of livestock manure on

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http://dx.doi.org/10.1016/j.agee.2017.01.012 0167-8809/© 2017 Elsevier B.V. All rights reserved. centralized biogas plants. Digestates produced as a by-product of biogas treatment of manure and organic wastes are rich in nutrients which should be recycled to agricultural land to meet the nutritional needs of crops (Möller and Müller, 2012; Nkoa, 2014).

When manure and organic waste are field-applied, local anaerobic zones will develop as a result of biological oxygen  $(O_2)$  consumption (Velthof and Mosquera, 2011; Zhu et al., 2015) and moisture retention by manure organic matter (Petersen et al., 2003). The  $O_2$  limitation around such hotspots can stimulate  $N_2O$  production *via* nitrification (Khalil et al., 2004) or denitrification (Coyne, 2008). Anaerobic digestion will partly remove easily degradable volatile solids (Nkoa, 2014), and this has implications for carbon (C) and nitrogen (N) turnover after field application; by reducing  $O_2$  demand as well as water retention, the potential for  $N_2O$  emissions compared to untreated manure may also decline.

Digestate properties vary considerably depending on origin of manure and organic co-substrates used for anaerobic digestion (Insam et al., 2015), and this has been shown to influence emissions of N<sub>2</sub>O after field application (Möller, 2015). However, reported effects of anaerobic digestion are mixed. For example, Petersen (1999) reported that application of a digestate to spring barley on a sandy loam soil reduced N<sub>2</sub>O emission relative to untreated manure or mineral fertilizer. Other studies did not find different N<sub>2</sub>O emissions from soil amended with untreated or digested cattle slurry (Amon et al., 2006; Clemens et al., 2006) or pig slurry (Thomsen et al., 2010). Rodhe et al. (2015) reported lower N<sub>2</sub>O emissions from digestate compared to untreated cattle slurry after field application to a silty loam soil. Thus, different manure materials in the same soil (Abubaker et al., 2013; Baral et al., 2016), or the same manure in different soils (Oenema et al., 2005; Abubaker et al., 2013), can produce varying patterns of N<sub>2</sub>O emissions, stressing the uncertainty of predicting effects of digestion on N<sub>2</sub>O emissions relative to untreated manure. Potentially a more consistent effect of anaerobic digestion would be found for yield-scaled N<sub>2</sub>O emissions (Van Groenigen et al., 2010). This is because digestates normally contain a higher proportion of N in mineral form available for plant uptake (Sommer and Husted, 1995; De Vries et al., 2012), and higher yields in combination with lower or comparable N<sub>2</sub>O emissions from digestates relative to untreated manure would thus generally result in lower yield-scaled emissions.

An agronomic index to evaluate the performance of digestates in crop production is nitrogen use efficiency (NUE; here defined as the percentage of total applied N recovered in above-ground parts), which is typically expressed as mineral N fertilizer replacement value (NFRV), where NFRV is the ratio of NUE of an alternative N source to NUE of mineral fertilizer. NUE and NFRV of digestates applied as fertilizer have been reported to increase compared to untreated slurry, thereby lowering yield-scaled N<sub>2</sub>O emissions (Lemke et al., 2012; Cavalli et al., 2016).

With a 30% share of the total grain yield in 2016, spring barley (Hordeum vulgare L.) is an important crop in Denmark. The objective of this study was to assess nitrous oxide (N<sub>2</sub>O) emissions and nitrogen use efficiency during growth of spring barley when fertilized with digestates and untreated manure, and to relate emission patterns to properties of soil and manure materials. One digestate was produced by anaerobic digestion of livestock manure and applied without further processing after storage. The other digestate consisted of digested and dewatered sewage sludge which, in accordance with current practice at the wastewater treatment plant, was mixed with cattle slurry and stored until field application. Untreated pig and cattle slurry were included as reference. The four manure materials were used as the only N source in a field plot experiment with the objective to assess N<sub>2</sub>O emissions, NUE and NFRV. Based on past experiments on this soil type (Petersen, 1999) we hypothesized that i) N supplied in digestates would contribute to reduce N<sub>2</sub>O emissions compared to untreated liquid manure, and ii) fertilizer N replacement value and crop yield would be related to mineral N availability.

#### 2. Methodology

#### 2.1. Site information

A field experiment was conducted at Foulumgaard experimental station (56° 49'N, 9°57'E) during spring-summer 2015. The soil is classified as loamy sand and contains 8.6% clay (<2  $\mu$ m), 12.0% silt (2–20  $\mu$ m), 46.6% fine sand (20–200  $\mu$ m), 32.8% coarse sand (>200  $\mu$ m), 18 g kg<sup>-1</sup> organic matter, 1.6 g kg<sup>-1</sup> total N, pH<sub>CaCl2</sub> 6.4 (Li et al., 2015), and 50  $\mu$ S cm<sup>-1</sup> electrical conductivity (Baral et al., 2016). Daily weather information was collected from a nearby (<200 m) climate station at the field site.

#### 2.2. Characterization of organic wastes

Four types of manure materials were applied as fertilizer in the field study: 1) Untreated pig slurry from finishers (treatment *PS*) and 2) untreated dairy cattle slurry (treatment *CS*), both materials originating from livestock production units at the experimental station, 3) a digestate obtained from Maabjerg BioEnergy, a large-scale centralized biogas facility in Holstebro, Denmark (treatment *MBD*), and 4) digested and dewatered sewage sludge from Fredericia Wastewater and Energy plant which, in accordance with current practice of the plant, had been stored together with untreated cattle slurry, here in a 2:1 mixture (w/w) based on volatile solids (treatment *CS+DDS*). The four materials had been stored in a pilot scale storage facility (Petersen et al., 2009) between June 2014 and April 2015.

The stored materials were mixed with a PTO powered agitator (Growi Electromixer; Tornado, Germany) and a subsample collected from each of duplicate storage tanks per treatment to determine slurry physico-chemical properties. Total N was determined by the Kjeldahl procedure (Kjeltec<sup>TM</sup> 2300; Foss, Sweden). Ammoniacal N in filtered suspensions of c. 2 g slurry or digestate in 100 mL demineralized water was determined with San-plus System auto-analyzer (Skalar Ltd., York, UK). Phosphorus and potassium content of the manure materials were determined using ICP-OES (Perkin Elmer, Optima 2100 DV) after digestion of 2-3 g in 10 mL nitric acid (HNO<sub>3</sub>) at 175 °C for 2 h. Slurry moisture and dry matter (DM) were determined from c. 20 g material by drying at 105 °C for 24h, and then for an additional 6h at 550 °C to determine ash content. Slurry pH and electrical conductivity (EC) were measured in a mixture of slurry and dem. water (1:2.5 w/w) using a pH/Conductivity meter (CyberScan PC 300; EUTECH Instruments, Singapore). The easily degradable fraction of VS

Table 1

Physical and chemical characteristics of slurry used in the spring barley field. Standard errors (n=4) are shown in parentheses. TN, total nitrogen; TAN, total ammoniacal nitrogen; P, phosphorus; K, potassium; EC, electrical conductivity; DM, dry matter; VS, volatile solids; VS<sub>d</sub>, easily degradable VS.

Manure type Treatment	Pig slurry <i>P</i> S	Digestate, Maabjerg MBD	Cattle slurry CS	Cattle slurry+digested sewage sludge CS+DDS
TN (g kg <sup><math>-1</math></sup> fw)	3.5 (<0.1)	4.3 (0.3)	3. 0 (0.2)	9.4 (0.8)
TAN (g kg <sup><math>-1</math></sup> fw)	2.3 (<0.1)	2.6 (0.1)	1.6 (0.1)	2.0 (0.1)
$P(gkg^{-1}fw)$	0.7 (<0.1)	1.4 (0.0)	0.6 (<0.1)	6.0 (<0.1)
$K (g kg^{-1} fw)$	2.2 (<0.1)	2.8 (0.0)	2.6 (<0.1)	2.1 (0.1)
pH <sub>1:2.5dH2O</sub>	7.6 (0.1)	8.3 (0.0)	8.0 (<0.1)	8.0 (<0.1)
$EC_{1:2.5dH2O}$ (mS cm <sup>-1</sup> )	3.0 (0.1)	3.4 (0.0)	2.2 (0.1)	2.4 (<0.1)
$DM (g kg^{-1} fw)$	36.8 (1.1)	42.6 (0.8)	53.5 (0.8)	113.9 (0.9)
VS (g kg <sup><math>-1</math></sup> fw)	26.1 (0.9)	27.5 (0.6)	39.5 (0.4)	70.5 (0.3)
$VS_d$ (kg kg <sup>-1</sup> VS)	0.60	0.13	0.15	0.05
C/N ratio <sup>a</sup>	9.3	6.9	11.9	4.1

<sup>a</sup> Assuming the total organic C (TOC) content of VS was 0.43 kg kg<sup>-1</sup> (Petersen et al., 2016), C/N ratios were calculated from ratios of TOC to total organic N=TN – TAN.

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