The Journal of Agricultural Science

cambridge.org/ags

Crops and Soils Research Paper

Cite this article: Pedersen BN, Christensen BT, Bechini L, Cavalli D, Eriksen J, Sørensen P (2020). Nitrogen fertilizer value of animal slurries with different proportions of liquid and solid fractions: A 3-year study under field conditions. *The Journal of Agricultural Science* **158**, 707–717. https://doi.org/10.1017/S0021859621000083

Received: 1 September 2020
Revised: 15 December 2020
Accepted: 17 January 2021
First published online: 23 February 2021

Keywords:
Cattle manure; nitrogen fertilizer replacement value; pig manure; residual value; slurry separation

Author for correspondence:
Peter Sørensen, E-mail: ps@agro.au.dk

Nitrogen fertilizer value of animal slurries with different proportions of liquid and solid fractions: A 3-year study under field conditions

Betina Nørgaard Pedersen[1], Bent T. Christensen[1], Luca Bechini[2], Daniele Cavalli[2], Jørgen Eriksen[1] and Peter Sørensen[1]

[1]Department of Agroecology, AU-Foulum, Aarhus University, Blichers Allé 20, 8830 Tjele, Denmark and [2]Dipartimento di Scienze Agrarie e Ambientali—Produzione, Territorio, Agroenergia, Università degli Studi di Milano, Milano, Italy

Abstract

The plant availability of manure nitrogen (N) is influenced by manure composition in the year of application whereas some studies indicate that the legacy effect in following years is independent of the composition. The plant availability of N in pig and cattle slurries with variable contents of particulate matter was determined in a 3-year field study. We separated cattle and a pig slurry into liquid and solid fractions by centrifugation. Slurry mixtures with varying proportions of solid and liquid fraction were applied to a loamy sand soil at similar NH4+-N rates in the first year. Yields and N offtake of spring barley and undersown perennial ryegrass were compared to plots receiving mineral N fertilizer. The first year N fertilizer replacement value (NFRV) of total N in slurry mixtures decreased with increasing proportion of solid fraction. The second and third season NFRV averaged 6.5% and 3.8% of total N, respectively, for cattle slurries, and 18% and 7.5% for pig slurries and was not related to the proportion of solid fraction. The estimated net N mineralization of residual organic N increased nearly linearly with growing degree days (GDD) with a rate of 0.0058%/GDD for cattle and 0.0116%/GDD for pig slurries at 2000–5000 GDD after application. In conclusion NFRV of slurry decreased with increasing proportion of solid fraction in the first year. In the second year, NFRV of pig slurry N was significantly higher than that of cattle slurry N and unaffected by proportion between solid and liquid fraction.

Introduction

On farms with intensive livestock production, land application of manure remains a dominant source of nitrogen (N) for crop production. In Denmark, the manure application rate to a given crop is usually defined by its content of ammoniacal-N, assuming that ammonium in manure is as effective as N applied in mineral fertilizers. In other parts of the world, a fraction of the organic N in manure is assumed to be available for the first crop after mineralization (Karimi *et al*., 2018). However, animal manures vary in chemical composition and other characteristics that may affect their N fertilizer value (Webb *et al*., 2013). Besides ammonium, animal manures contain organically bound N, the amount of which depends on animal species, feeding, housing system (including beddings) and storage conditions before land application (Sørensen *et al*., 2019). Upon mineralization, the organic N in manure may contribute mineral N for subsequent crop uptake but also for potential N loss via nitrate leaching or denitrification. Loss of ammonia by volatilization remains critical to the fertilizer value of manure N for the first crop. However, direct injection of liquid manure or immediate incorporation of solid manure can reduce ammonia volatilization to very low levels (Sommer and Hutchings, 2001). To maximize the N use efficiency (NUE) and minimize negative environmental impacts, the effect derived from mineralization of manure N in the years that follow application has to be accounted for.

In the year of amendment, immobilization of ammoniacal-N and mineralization of labile organic N occur simultaneously and affect the N fertilizer value of the manure. The balance between these processes, termed net N mineralization, often relates to quality parameters such as the C/N ratio (Chadwick *et al*., 2000; Peters and Jensen, 2011), which in turn links to the organic matter composition of the manure. In the years following a single manure application, the residual N effect is typically small and therefore difficult to quantify. For land exposed to frequent annual manure applications, however, the cumulated residual N effects may become significant and should be quantified to allow for adjustment of fresh N inputs. Residual effects of manure application vary as illustrated by Chalk *et al*. (2020) in a review of studies based on ^{15}N-labelled manures. Of the total ^{15}N applied, crop recovery (also termed NUE) from various pig, cattle and sheep manures ranged from 1.8 to 15% in the first residual year; in the second residual year the recovery ranged from 1 to 3.7%.

Some studies on the value of manure N in crop production have relied on determination of NUE. To be more readily applicable in practical farming, the NUE of animal manure can be converted into the mineral N fertilizer replacement value (NFRV). The NFRV represents the amount of mineral N fertilizer that can be substituted by a given quantity of N in animal manure (Webb *et al*., 2013). Compared with NUE, however, the determination of NFRV is experimentally more demanding as one or more reference treatments with mineral N fertilizer using the same crop under comparable soil and atmospheric conditions are required.

Results reported by Jensen *et al.* (1999) indicated that the residual effects of manures are mainly determined by the input of total N with manures, whereas other studies have indicated that other factors influence the residual effect (e.g. Sørensen *et al*., 2017 and Chalk *et al*., 2020). The objectives of the present study were: (a) to examine the effect of solid material content and thus C/N ratio, in cattle and pig slurries on manure N fertilizer value in the application year and the following 2 years, and (b) to quantify the mineralization rate of residual organic manure N in soil following application of different manure qualities in relation to climatic conditions (growing degree days (GDD)).

Material and methods

Site and soil

Field micro-plots were established in 2017 at Research Centre Foulum (56°30′N, 09°35′E, elevation 41 m above sea level), Aarhus University, Denmark, by inserting polyvinyl chloride (PVC) cylinders (diameter, 30 cm; length 30 cm) into the soil to a depth of 25 cm. The soil is a sandy loam with 80 g clay/kg (<2 μm), 125 g silt/kg (2–20 μm), 760 g sand/kg (20–2000 μm), 35 g organic matter/kg and pH (H_2O) 6.8 (Sørensen *et al*., 2003). Altogether, 60 cylinders were installed in two rows with 0.5 m between rows and between cylinders within a row. The field received manures regularly until 2015.

Animal manures

Two animal manures, a dairy cattle slurry stored outdoors in a covered slurry tank for several months before sampling, and a pig slurry retrieved directly from underneath a stable facility with 7–30 kg piglets, were available for this study. The manures were separated into two fractions by centrifugation at an acceleration of 4600 g for 4 and 2 min for pig and cattle slurry, respectively. The supernatant (liquid fraction, L) was isolated from the solid fraction (S) by decantation. Table 1 shows the chemical composition of the pig and cattle slurry fractions and the proportion between solid and liquid fractions after centrifugation.

Subsequently, liquid and solid fractions were recombined to create five cattle and five pig slurry mixtures, targeting mixtures for which 0, 25, 50, 75 and 100% of the NH_4^+ originated from the solid fraction. Table 2 shows the proportion of solid and liquid fraction in each mixture and the resulting properties of the slurry mixtures. With this approach, the treatments also differed in amounts of slurry dry matter, fibrous organic matter and organic N.

Experimental setup

Besides the ten slurry treatments, the experiment included five reference treatments dressed with increasing rates of mineral N fertilizer. The treatments were organized in a randomized design with four blocks. The experiment lasted 3 years (2017, 2018 and 2019) with slurry mixtures applied in spring 2017 only. The application rate corresponded to 150 kg NH_4^+-N/ha for cattle slurries and 142 kg NH_4^+-N/ha for pig slurries (Table 2), based on preliminary analyses.

The slurry treatments received no mineral N fertilizer throughout the experiment. The five reference treatments with mineral N fertilizer received 0, 100, 150, 200 and 250 kg N/ha in the spring 2017 as ammonium-nitrate solution. These treatments received another 0, 50, 75, 100 and 150 kg N/ha in the spring 2018 and 2019 and the same rates after each of the first three cuts in 2018 and two cuts in 2019. Total N fertilizer applications were thus 0, 200, 300, 400 and 600 kg N/ha in 2018 and 0, 150, 225, 300 and 450 kg N/ha in 2019.

The slurry mixtures were applied on 2 May 2017 by simulating injection to 10 cm depth. The 0–5 cm of soil was removed from the cylinder, the slurry placed in a 5 cm deep furrow and the slurry band then covered with soil immediately after. A similar procedure was used for mineral N fertilizer treatments. The following day, spring barley (*Hordeum vulgare* L., cv. KWS Irina) was planted at 3 cm soil depth with a row spacing of 12 cm (368 seeds/m^2) and undersown with perennial ryegrass (*Lolium perenne* L., cv. Calvano). The grass seeds were surface-applied (8 kg seeds/ha) and lightly incorporated into the soil. Subsequently, a nutrient solution containing P, K, S, Ca and Mg at rates corresponding to 50, 198, 17, 100 and 50 kg/ha was added. Another nutrient solution including micronutrients (Mn, Zn, Mo, Cu, B and Co) was added, and similar nutrient solutions were added again in spring 2018 and 2019. The area surrounding the plots received standard rates of mineral fertilizers and was seeded to spring barley.

The spring barley was harvested as a whole-crop on 18–19 July 2017 and one cut of grass taken on 23 October 2017. In 2018, the grass crop was harvested four times (31 May, 11 July, 6 September and 24 October). In 2019, three cuts were taken (12 June, 7 July and 9 September), leaving a stubble of approximately 5 cm after each cut.

Climate

The mean air temperature during the growing season (April–October) was 12.3°C in 2017, 14.2°C in 2018 and 12.5°C in 2019 (1961–1990 mean; 11.6°C). Precipitation during this period was 564, 340 and 562 mm in 2017, 2018 and 2019, respectively (1961–1990 mean; 402 mm). In the warm and dry spring and summer of 2018, irrigation water was added to the cylinders three times (140 mm in total). Figure 1 shows monthly precipitation and mean temperatures.

Analytical methods

To establish the application rates of slurries, the solid and liquid fractions were subject to preliminary analyses for total N and ammoniacal-N after separation but before mixing. Total N was measured by Kjeldahl digestion (Tecator Kjeltec Auto 1030) and ammoniacal-N was determined by an automated distillation-titration method (Sommer *et al*., 1992). Following 2 months of storage at 2°C, the liquid and solid slurry fractions were re-analysed for total N and ammoniacal-N, and concentrations of P, K and S determined by ICP-OES (Inductively Coupled Plasma – Optical Emission Spectrometry). Total C content was determined by high-temperature dry combustion.

Table 1. Chemical composition of the solid and liquid fractions of cattle and pig slurry

	Cattle		Pig	
Property	Liquid	Solid	Liquid	Solid
Dry matter (g/kg)	30	152	29	239
Total-N (g/kg)	3.0	4.6	3.8	9.7
NH_4^+-N (g/kg)	1.9 (1.9)	2.4 (2.5)	2.2 (2.5)	2.2 (3.4)
NH_4^+-N /Total-N	0.62	0.52	0.59	0.23
pH	7.8	9.9	6.3	6.3
Carbon (% DM)	44	43	41	47
Phosphorus (g/kg)	0.1	2.0	0.7	3.6
Potassium (g/kg)	3.5	3.4	2.3	2.3
Sulphur (g/kg)	0.2	0.9	0.6	1.5
C/N	4.4	14.3	3.1	11.6
C/Organic N	11.8	30.1	7.6	15.0
Proportion (% of wet weight)	72	28	74	26

Numbers in parentheses are contents of ammonium N in slurry fractions measured after 2 months of storage at 2°C. Proportion indicates the % of the unseparated slurry isolated as liquid and solid fraction after separation by centrifugation and decantation.

The barley and grass biomasses were chopped and subsamples dried at 60°C for 24 h to determine dry matter content. Total N of plant material was measured by high-temperature dry combustion.

Calculations

Nitrogen uptake efficiency of mineral N fertilizer (NUE_{MN}) was determined by plotting N uptake in the grass (plus barley in 2017) against total N amendment.Nitrogen uptake efficiency of slurry mixtures (NUE_{slurry}) was calculated as:

$$NUE_{slurry} = \frac{(Nupt_{Slurry}\text{-}Nupt_{0N})}{(Napplication_{slurry})} \times 100\ \%$$

where $Nupt_{Slurry}$ is the N uptake in the slurry treatment and $Nupt_{0N}$ is the N uptake in the unfertilized reference treatment. $Napplication_{slurry}$ is the N applied in the slurry treatments in 2017.

The NFRV was calculated as:

$$NFRV = \frac{NUE_{slurry}}{NUE_{MN}} \times 100\ \%$$

For calculating NFRV in 2018 and 2019, NUE_{slurry} was calculated based on total N application in 2017, while NUE_{MN} was calculated based on the mineral N amendment in 2018 and 2019, respectively.

Assuming that N mineralized from slurry and N added in mineral fertilizer is taken up by plants with the same efficiency, NFRV provides an estimate of net N mineralized from the slurry in 2018 and 2019 (Sørensen *et al.*, 2017).

Mineralization of slurry N was related to residual manure N left in soil after harvest of the first barley crop estimated as:

$$\text{Residual } N(\%\text{ of total applied } N) = 100 - \ \%\text{NFRV in barley}.$$

By this calculation it is assumed that the proportion of unknown N losses (gaseous or leaching losses) were similar from applied mineral N and N in slurry mixtures.

Based on temperature recordings at Research Centre Foulum, thermal time after application of animal slurries was expressed as GDD based on air temperatures above 5°C where each day is multiplied with temperature minus 5°C (Bhogal *et al.*, 2016).

Statistical analysis

Statistical analysis was carried out in R (R Core Team, 2018). Post hoc analysis was carried out with the emmeans package. A significance level of $P < 0.05$ was used throughout. Based on visual inspection of quantile-quantile-plots (QQ-plots), data were found to have a normal distribution and the variance homogeneity was evaluated by inspection of residuals.

Mineral N reference curves were established using linear regression with N uptake as response variable and N application as explanatory variable. A linear mixed model was defined for each of the four response variables: dry matter, N uptake, NUE and NFRV for slurry treatments with year, slurry mixture (proportion of NH_4-N from solid fraction) and manure type as fixed effects (including interactions) and plot and block as random effects (Bates *et al.*, 2015). Pairwise comparisons of means within the year and manure type were conducted using the Tukey's honestly significant difference (HSD) test.

Linear models relating NUE to a ratio of ammonium from solid fraction, a ratio of organic N from solid fraction, C/N ratio, C/Organic N ratio and ammonium to total N ratio were compared using the Akaike's information criterion (AIC) within each year. The AIC is a tool used to compare models and describes the relative amount of lost information. Therefore, the lower the AIC the better the model. Nitrogen mineralization as a function of GDD was analysed using linear regression with GDD, slurry mixture (proportion of NH_4-N from solid fraction) and manure type as explanatory variables.

Table 2. Properties of the cattle and pig liquid–solid slurry mixtures and field amendment rates

		Mixture properties									Field amendment rates	
Mixture	Slurry type	NH_4^+ derived from solid fraction (%)	Org N derived from solid fraction (%)	Mass from solid faction (%)	NH_4^+-N (g/kg)	Total N (g/kg)	Total C (g/kg)	NH_4^+-N /Total N	C/N	C/Org N	NH_4^+-N (kg/ha)	Total N (kg/ha)
L100 : S0	Cattle	0	0	0	1.86	2.98	13.2	0.63	4.4	11.8	150	240
L75 : S25	Cattle	25	34	21	2.00	3.38	26.2	0.59	7.8	19.0	150	252
L50 : S50	Cattle	50	60	44	2.13	3.77	39.3	0.56	10.4	23.9	150	263
L25 : S75	Cattle	75	82	70	2.26	4.17	52.3	0.54	12.6	27.4	150	275
L0S100	Cattle	100	100	100	2.39	4.56	65.4	0.52	14.3	30.1	150	286
L100 : S0	Pig	0	0	0	2.22	3.79	11.9	0.59	3.1	7.6	142	242
L75 : S25	Pig	25	62	25	2.21	5.27	37.0	0.42	7.0	12.1	142	338
L50 : S50	Pig	50	83	50	2.21	6.75	62.1	0.33	9.2	13.7	142	434
L25 : S75	Pig	75	94	75	2.20	8.23	87.2	0.27	10.6	14.5	142	529
L0S100	Pig	100	100	100	2.20	9.71	112.3	0.23	11.6	15.0	142	625

L = liquid fraction and S = solid fraction.

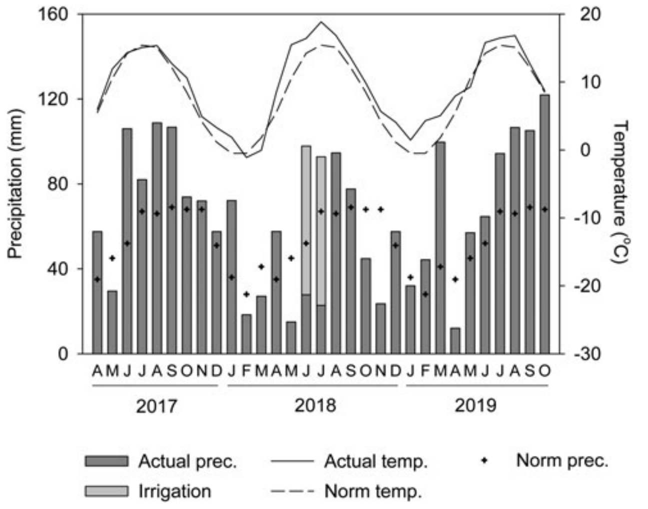

Fig. 1. Monthly precipitation and irrigation in mm (grey bars) from April 2017 to October 2019 and monthly average precipitation (1961–1990, black lines). Actual and mean monthly temperatures in ^{0}C (full line with full circles and dotted line with open circles, respectively) for the same period.

Results

Mineral N fertilizer response

Figure 2 shows total dry matter yield and N uptake in the reference treatments with mineral N fertilizers. For all 3 years, dry matter yield and N uptake increased linearly with N application rate. NUE_{MN} was 79% in 2017, declining to 55% in 2018 and 37% in 2019.

For the mineral N fertilizer treatments, NUE_{MN} was calculated for each harvest (Table 3). NUE_{MN} was high for the spring barley grown in 2017 (80%). The grass cut taken in autumn 2017 was not fertilized with N and NUE_{MN} could not be established. In 2018 and 2019, the first grass cut showed the greatest NUE_{MN} and plant N uptake at 0N fertilizer. Plant N uptake for 0N treatments and NUE_{MN} were small for the last two cuts in 2019. Without N fertilization, cumulated plant N uptake was 77 kg N/ha in 2017, 69 kg N/ha in 2018 and 33 kg N/ha in 2019.

Fertilizer value of slurries in the year of application (2017)

Dry matter yields of the barley plus the grass cut in 2017 (Fig. 3(*a*)) were similar for all cattle slurry mixtures, although the L100 : S0 and L0 : S100 slurries tended to produce slightly smaller yields. Yields were higher for pig than for cattle slurries and appeared to increase with increasing proportions of solid fraction from pigs. An increase in N uptake with increasing proportion of solid fraction was seen for pig but not for cattle slurries (Fig. 3(*b*)), however, total N application also increased with increasing proportion of solid fraction. The NUE_{slurry} (Fig. 3(*c*)) related to the total N amendment (Table 2) decreased when the proportion of solid fraction increased. This was true for the pig as well as cattle slurry when excluding the L100 : S0 cattle slurry. For both cattle and pig slurry, the NUE_{slurry} of L75 : S25 was significantly higher than that of L25 : S75 and L0 : S100.

The linear relationships between NUE_{slurry} and the proportion of ammonium N or organic N derived from solid fraction, the C/N ratio, the ratio C/organic N, and ammonium to total N ratio were compared using AIC. The ratio of ammonium originating from the solid fraction described the relationship best (Table 4). Generally, NUE_{slurry} of cattle slurry mixtures were poorly predicted by all the tested parameters. For the pig slurry mixtures, NUE_{slurry} was fairly well predicted by C/N and ammonium to total N ratio.

In the first barley crop, NFRV related to total N application similarly decreased with increasing proportion of solid fraction (Table 5) with a few exceptions such as L100 : S0 *v.* L75 : S25 from cattle. The largest difference between cattle and pig slurries was observed for mixtures containing only liquid fractions. With no solid fraction present, NFRV was 58% for cattle and 70% for pig slurry. Overall NFRV of the pig slurries was significantly higher than the cattle slurries.

Fertilizer value of slurries in the residual years (2018 and 2019)

Figures 4(*a*) and (*b*) show plant dry matter yields and N uptake in the two residual years. Yields and N uptake were considerably smaller in 2019 than in 2018 and this was also true for the reference treatments with mineral N fertilizer additions (Fig. 2). In 2018, no significant differences in dry matter yields and N uptake were seen for treatments with cattle slurries regardless of mixing ratio between solid and liquid fractions. In contrast, yields and N uptake were greater for pig slurries with more than 50% of the ammonium originating from solid fraction than for pig slurries with less solid fraction. In the second residual year (2019), yields and N uptake were similar for all treatments. When N uptake in 2019 was related to the total N applied in 2017 to calculate NUE,

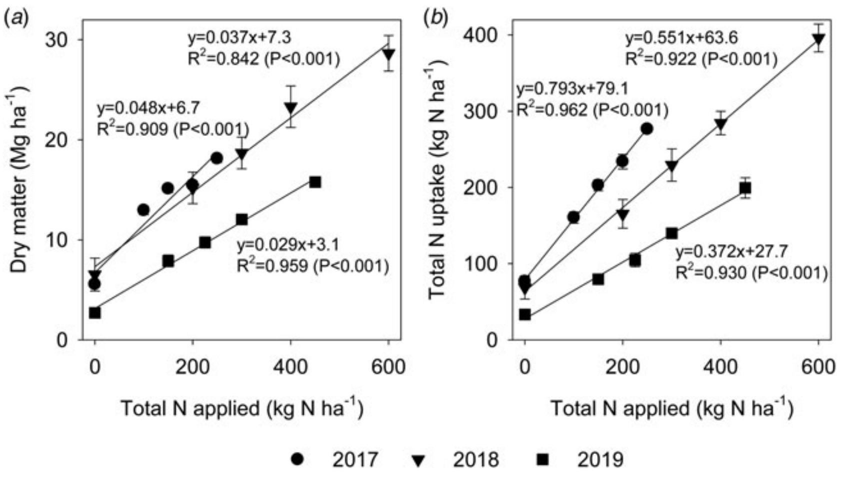

Fig. 2. Dry matter yield (a) and total N uptake (b) in mineral N reference treatments shown for 2017 (barley + one grass cut), 2018 (four grass cuts) and 2019 (three grass cuts) related to a total annual mineral N application rate. Error bars indicate standard error (n = 4).

Table 3. Nitrogen uptake efficiency of mineral N fertilizer (NUE_{MN}) for each harvest based on a linear regression between N application rate and crop N uptake

Year	Harvest/cut	NUE_{MN} (%)	*P* value	R^2	N uptake at 0N (kg N/ha)
2017	Spring barley	80.4	<0.001	−0.973	54.1
	First grass cut	–	–		22.5
2018	First grass cut	65.4	<0.001	−0.633	36.5
	Second grass cut	43.0	<0.001	−0.940	11.6
	Third grass cut	60.0	<0.001	−0.884	13.0
	Fourth grass cut	51.9	<0.001	−0.812	7.6
2019	First grass cut	53.8	<0.001	−0.926	13.6
	Second grass cut	29.6	<0.001	−0.872	9.4
	Third grass cut	28.3	<0.001	−0.736	10.4

The first grass cut after barley harvest in 2017 was not fertilized with N. Crop N uptake at unfertilized reference plots (0N) is also shown.

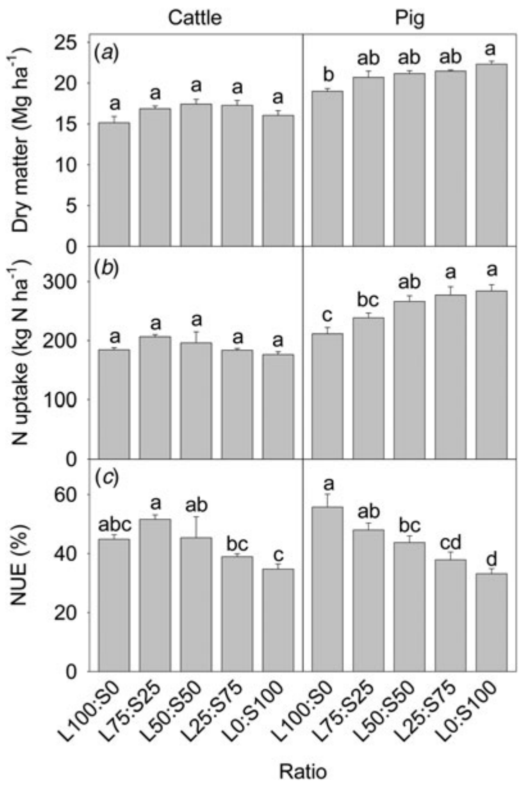

Fig. 3. Dry matter yield of barley plus grass (a), crop N uptake (b) and N uptake efficiency (NUE_{slurry}) for total N applied in pig and cattle slurry mixtures (c) in 2017. Explanation of mixtures is given in Table 2. Bars indicate means and error bars show standard errors, and letters indicate significant differences within each slurry type (cattle and pig) analysed with a Tukey test ($n = 4$).

no significant differences were seen between the slurry mixtures from both cattle and pigs (Fig. 4(*c*)). The NUE_{slurry} for cattle and pig slurries averaged 4% (3–5%) and 10% (6–16%) in the first residual year (2018). For the second residual year (2019), NUE_{slurry} was reduced to 0–5%, with an average of 1% for cattle slurries and 3% for pig slurries.

No significant linear relationships were found in 2018 and 2019 between NUE_{slurry} and proportion of ammonium derived from the solid fraction, organic N from solid fraction, C/N ratio, the ratios C/organic N, or ammonium to total N ratio (data not shown).

In 2018, the NFRV related to total N application averaged 6.5% (6–8%) for cattle slurries and 18% (11–29%) for pig slurries (Table 5). The NFRV in 2019 ranged from 1 to 9% for cattle (mean 3.8%) and from 2 to 13% for pig slurries (mean 7.5%).

Cumulated nitrogen uptake in slurry treatments

Table 6 shows the cumulated plant N uptake throughout the experimental period. The N uptake did not differ significantly among cattle slurry treatments. Generally, total N uptake was higher for the pig than for cattle slurries. Treatments receiving pig slurries with 50% or more solid fraction showed significantly higher plant N uptake than treatments with a less solid fraction. When the N uptake is related to the total N input (NUE_{slurry}), differences between pig and cattle slurry diminished. Most differences in NUE_{slurry} among different ratios were not significant, although NUE_{slurry} tended to be smallest when slurries only contained the solid fraction. Figure 5 shows that most of the differences in cumulated NUE_{slurry} among cattle slurries were established already in 2017 at barley harvest. For the pig slurry mixtures, the differences in cumulated NUE decreased over time if we disregard the exceptional L50 : S50 treatment.

Availability of residual nitrogen and growing degree days

The residual manure N left after barley harvest was estimated as total N applied minus NFRV in the barley crop.

The net mineralization of residual manure N during the following 2 years was estimated based on the NFRV calculated for each grass cut, assuming no mineral N left at barley harvest. Thus, we ascribe fertilizer effects seen after barley harvest to mineralization of residual organic N, including re-mineralization of previously immobilized ammoniacal N. Mineral N fertilizer was not applied to the first grass cut in autumn 2017, and we assume a NUE of 49% of mineralized N, based on a previous study on the same soil type and location (Li *et al*., 2015), to calculate net N mineralization in the first autumn.

Figure 6 shows the relationship between GDD and cumulated net N mineralization, calculated as a percentage of residual slurry N estimated to remain in soil after barley harvest in 2017. There was a large variation in net N mineralization of residual N estimated for the period until the second grass cut (one in 2017 and one in 2018) both within and between treatments. This

Table 4. Relationship between nitrogen uptake efficiency in the first year barley plus grass crop from cattle and pig slurry mixtures (Y, NUE_{slurry}) and NH_4-N proportion from solid fraction (%), C/N ratio, C/organic N ratio, organic N proportion from solid fraction (%) and NH_4-N/total N ratio

	Cattle				Pig			
Parameter (*x*)	Linear regression	*P* value	R^2	AIC	Linear regression	*P* value	R^2	AIC
NH_4^+-N from solid fraction	$Y = -0.14 \times + 50$	0.005	0.376	114	$Y = -0.22 \times + 55$	<0.001	0.699	126
C/N ratio	$Y = -1.28 \times + 56$	0.012	0.312	115	$Y = -2.56 \times + 65$	<0.001	0.676	128
C/organic N ratio	$Y = -0.66 \times + 58$	0.019	0.270	116	$Y = -2.75 \times + 78$	<0.001	0.614	132
Organic N from solid fraction	$Y = -0.13 \times + 50$	0.012	0.312	115	$Y = -0.20 \times + 57$	<0.001	0.612	132
NH_4^+-N/total N ratio	$Y = 112.9 \times -21$	0.015	0.290	116	$Y = 59.9 \times + 21$	<0.001	0.674	128

Table 5. Nitrogen fertilizer replacement value (NFRV) of slurry mixtures measured over three growing seasons related to total N applied in 2017 and to residual manure N in soil after barley harvest

	2017 (barley)		2018 (grass)				2019 (grass)			
	Cattle	Pig	Cattle		Pig		Cattle		Pig	
Mixture	% of total *N*	% of total *N*	% of total *N*	% of residual *N*	% of total *N*	% of residual *N*	% of total *N*	% of residual *N*	% of total *N*	% of residual *N*
L100 : S0	58 ab	70 a	6 a	12 a	11 b	33 a	2 a	5 a	2 a	6 a
L75 : S25	66 a	57 b	8 a	24 a	15 ab	33 a	6 a	18 a	8 a	19 a
L50 : S50	55 bc	48 c	6 a	14 a	29 a	54 a	9 a	20 a	13 a	25 a
L25 : S75	50 bc	39 d	7 a	14 a	19 ab	30 a	3 a	6 a	6 a	10 a
L0 : S100	46 c	36 d	6 a	10 a	16 ab	25 a	1 a	2 a	8 a	12 a
Average	55 A	50 B	7 A	15 B	18 B	35 A	4 A	7 A	8 A	15 A

No significant interactions between mixture and slurry type ($P < 0.05$).
Explanation of mixtures is given in Table 2. Small letters indicate significant differences within slurry type (cattle and pig) and year, and different capital letters indicate a significant difference between averages of cattle and pig slurries within each year analysed with a Tukey test ($n = 4$).

variation is reflected in the cumulated numbers and the error bars in Fig. 6. The average mineralization rate for pig slurries was 0.0203%/GDD in the period 0–2000 GDD. From 2000 GDD and throughout the experiment, a nearly linear relationship was observed between GDD and cumulated net N mineralization. In the following, we assumed a linear relationship as a proxy even though a slight decrease in N mineralization rate appeared after 4000 GDD for some of the slurries. During 2018 and 2019, the average mineralization rate of residual N was 0.0059%/GDD for cattle mixtures and 0.0105%/GDD for pig mixtures. Excluding the deviant L50 : S50 treatment, the mineralization rate of organic N from pig slurries became 0.0088%/GDD. Averaged across 2018 and 2019 and all slurry mixtures, the N mineralization rate after 2000 GDD was 0.0084%/GDD.

The period from barley harvest to the first grass cut in autumn 2017 showed a decrease in NFRV corresponding to 3.5% of the residual N in treatments with cattle slurries, indicating a slight net N immobilization due to the cattle slurry in this period (Fig. 6). In 2018, the average net mineralization from cattle slurry mixtures was equivalent to 15% of the residual slurry N and in 2019 the mineralization was equivalent to 7% of residual N. For treatments with pig slurries, the average mineralization in autumn 2017 (Fig. 6) was equivalent to 13% of the residual slurry N. In 2018, the average mineralization from pig slurries was equivalent to 35% of the residual pig slurry N in soil and in 2019 equivalent to 13% of the residual N.

Discussion

Fertilizer value of slurries in the year of application

In the year of application (2017), the NFRV ranged from 46 to 66% for cattle slurries and from 36 to 70% for pig slurries (Table 5). Except for the slurry with no solid fraction, the differences between pig and cattle slurries with similar proportions of liquid and solid fractions were small. Our first-year effect of N added with slurry is in accordance with Sørensen *et al.* (2019) who ascribe a potential NFRV of 40–80% to pig slurry and 35–65% to cattle slurry and report the availability of N to be lower for solid than for liquid fractions.

Sørensen and Thomsen (2005) did a similar separation of pig slurry after the slurry had been stored anaerobically for a few weeks. Using the same approach as here, they found NFRVs of 50, 98 and 81% for the solid fraction, the liquid fraction and the unseparated slurry, respectively. Thus, their first-year fertilizer values were somewhat higher than in the present study, especially for the liquid fraction. A reason for this could be that the liquid fraction contained more decomposable carbon in our study as the pig slurry was not stored prior to separation, which would cause extra N immobilization by microbial decomposition and a lower N fertilizer value for the first crop. The pig slurry used by Sørensen and Thomsen (2005) was ^{15}N-labelled, and when they calculated the NFRV using the ^{15}N recovery in the crop they found slightly lower fertilizer values of 48, 91 and 75% for the

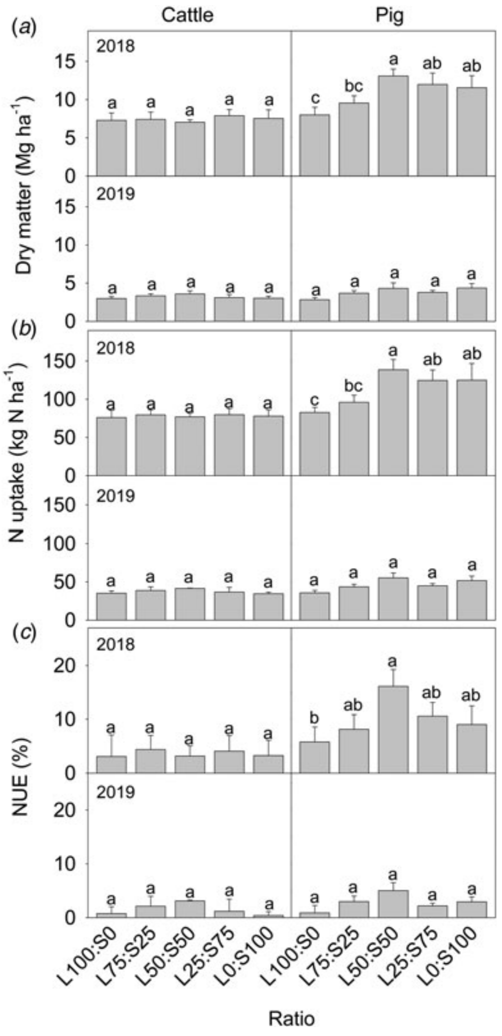

Fig. 4. Dry matter yield in the grass (a), crop N uptake (b) and NUE_{slurry} (c) after application of different pig and cattle slurry mixtures determined for 2018 and 2019 and based on total slurry N applied in 2017. Explanations of mixtures are given in Table 2. Bars indicate means and error bars show standard error. Letters indicate significant differences within slurry type (cattle and pig) and year, analysed with a Tukey test ($n = 4$).

solid fraction, the liquid fraction and the unseparated slurry, respectively. These estimates of NFRV for the solid fraction were lower with our pig solid fraction (36%) and with our pig liquid fraction (70%).

Presumably most of the fibrous solid fraction derived from faeces and in the year of application, Jensen *et al.* (1999) found NFRV values of 15% for ^{15}N-labelled sheep faeces that were mixed with straw and urine and applied to soil planted to spring barley and undersown with grass. Using a similar experimental set-up, but using winter wheat as a test crop, Bosshard *et al.* (2009) observed recoveries of ^{15}N in wheat of 10% for faeces and 47% for mineral N fertilizer, providing NFRV of 21% for the faecal N. The higher NFRV of 46% for the cattle solid fraction compared to that of cattle faecal N indicates that a significant part of the solid fraction derived from urine with a much higher N availability.

Sørensen and Thomsen (2005) observed that NFRV exceeded the ammonium content of pig slurry, indicating a net mineralization of organic pig slurry N during the year of application. We also saw net N mineralization after barley harvest for pig, but not for cattle slurries. However, this difference may derive from the different pre-experiment storage period of the two slurries. The liquid and solid fractions of the slurries were mixed based on the ammonium and total N contents determined in the preliminary analyses shortly after slurry separation. While the cattle slurry had been stored for several months before used in this experiment, the available pig slurry was retrieved freshly from the piglet stable facility and applied in the field after a few days of storage. To get a measure of easily mineralizable organic N in the slurry the cattle and pig slurry fractions were therefore stored anaerobically for 2 months at 2°C and re-analysed. The subsequent analyses showed an increase in ammonium content of the pig solid and liquid fractions compared to the preliminary analyses, but no significant increase for the cattle fractions (Table 1). After the 2-month storage period, the ammoniacal-N content in the pig slurry solid fraction increased from 2.2 to 3.4 g/kg. Previous studies showed that anaerobic storage of slurry during a few months had insignificant influence on net N release following application to soil (Sørensen, 1998).

The NFRV was found to be related to the proportion of solid fraction, but the C/N ratio was also ascribed a considerable part of

Table 6. Cumulated apparent recovery of slurry N (sum of 2017, 2018 and 2019) expressed as kg N/ha (after subtraction of crop N uptake in 0N plots) and nitrogen uptake efficiency (NUE_{slurry}) based on slurry total N applied in 2017

	Cattle		Pig	
Mixture	Cumulated slurry N uptake (kg N/ha)	Cumulated NUE_{slurry} (%)	Cumulated slurry N uptake (kg N/ha)	Cumulated NUE_{slurry} (%)
L100 : S0	120 a	49 ab	151 b	62 a
L75 : S25	149 a	58 a	200 b	59 ab
L50 : S50	139 a	52 ab	281 a	65 a
L25 : S75	121 a	44 ab	268 a	51 ab
L0 : S100	110 a	38 b	282 a	45 b
Average	137 A	52 A	245 B	59 B

No significant interactions between mixture and slurry type ($P < 0.05$).
Explanation of mixtures is given in Table 2. Small letters indicate significant differences within slurry type (cattle and pig), and different capital letters indicate a significant difference between averages of cattle and pig slurries by a Tukey test ($n = 4$).

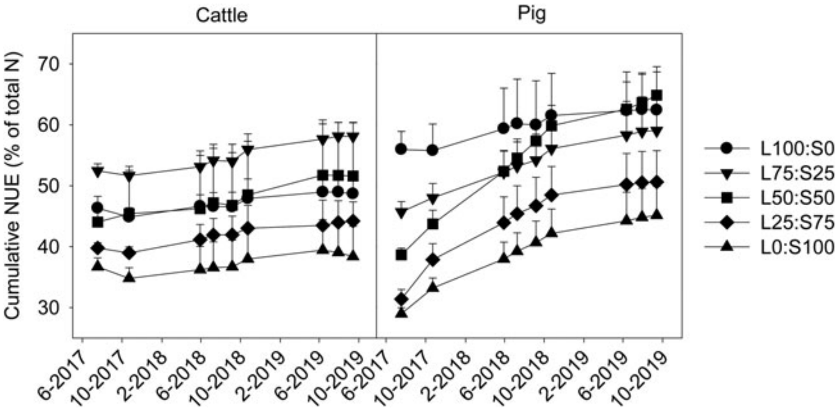

Fig. 5. Cumulated N uptake efficiency (NUE$_{slurry}$) of total N applied in slurry mixtures in 2017 during three cropping seasons. Error bars show standard errors ($n = 4$).

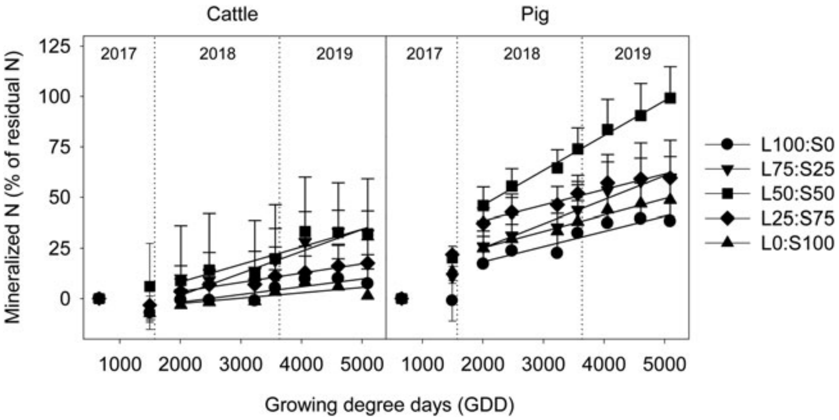

Fig. 6. Cumulated net mineralization of residual organic manure N left in the soil after harvest of the first barley crop in treatments receiving slurry mixtures in 2017 as a function of growing degree days (GDD) since application with a base temperature of 5°C. Mineralization of N taking place before the first grass cut in 2018 is not included in the regressions. Error bars show standard errors ($n = 4$).

the variation in NFRV (Table 4). Previous studies have found the C/N ratio to be a good indicator of mineralization potentials. Webb *et al.* (2013) report a strong negative correlation between NFRV and C/N ratio based on slurries from experiments with pigs and cattle subjected to different diets. For a spring barley crop, NFRV ranged from 90% for slurry with a C/N ratio of 2 to 60% for slurry with a C/N ratio of 13. A clear impact of the C/N ratio was also shown by Reijs *et al.* (2007) and Qian and Schoenau (2002) for a range of different animal manures. Differences in C/N ratio could thus be one explanation for differences among slurry mixtures in first year N fertilizer effect. As shown in Table 2, the C/N ratio of cattle as well as pig slurry mixtures increased with increasing proportion of solid fraction.

The fast N mineralization rate in the first autumn from the pig slurry mixtures may have environmental implications. If the soil is kept vegetation-free in autumn, nitrate leaching may increase whereas there may be a fertilizer effect when the soil is covered with a crop with a long growing season. If pig slurry is applied to crops with a short growing season, the establishment of the following cover crop would be recommendable to reduce the risk of nitrate leaching.

Residual fertilizer value of slurries

The N uptake in grass in 2018 due to mineralization of manure N resulted in an average NUE$_{slurry}$ of 4% and 10% of total N applied in 2017 for cattle and pig slurries, respectively. The N effect was smaller in 2019 with corresponding NUE$_{slurry}$ values of 1% and 3% of the total N applied in 2017 (Fig. 4(*c*)). For ^{15}N-labelled dairy manure applied to maize, Cusick *et al.* (2006) recovered 4–8% of the ^{15}N in the first residual year and 1–3% in the second residual year. Corresponding recoveries were 3% and 1.4% for sheep faeces and urine using soybeans and maize as test crops, respectively (Bosshard *et al.*, 2009). For sheep manures composed of ^{15}N-labelled faeces, urine and straw components and applied to a spring barley crop followed by grass, Jensen *et al.* (1999) recorded similar N recoveries for all three components (3.7% in the first residual and 1.4% in the second residual year). For physically separated and ^{15}N-labelled pig slurry, Sørensen and Thomsen (2005) found recoveries of 3.5% for the dry matter rich fraction and 2.3% for the liquid fraction in a barley crop in the first residual year.

Assuming a 50% recovery of ^{15}N-labelled mineral fertilizers (Chalk *et al.*, 2020), the residual N effects of the ^{15}N-labelled animal manures above convert to NFRV ranging from 6 to 16% in the first residual year and 3–6% in the second residual year. The smallest values were for urine and liquid manure fractions. In accordance with our results, pig slurry tends to provide larger first-year residual effects than manure derived from ruminants. The NFRV for cattle slurry mixtures was on average 7% in 2018 and 4% in 2019 and aligns with Klausner *et al.* (1994) who found NFRV of 9, 3, 3 and 2% for the first, second, third and fourth residual year, respectively, for dairy manure applied to maize. However, we observed considerably higher NFRV for total N added with pig slurries (18% in 2018 and 8% in 2019, Table 5). Sørensen and Amato (2002) similarly found a high NFRV in barley plus a cover crop in the year after application of pig slurry, equivalent to 11% of the total N applied, on the same soil type as the present study. A much lower residual effect, equivalent to 5% of the total N input, was observed on more clayey soil.

According to the empirical N mineralization model developed by Sørensen *et al.* (2017) based on measured NFRV, 17 and 8% of organic N input in cattle slurry becomes mineralized in the first and the second residual year, respectively. This corresponds well to our results when NFRV is related to residual organic N for cattle slurries, showing that 15% of the residual organic N was mineralized in 2018 and further 7% in 2019 (Table 5). For pig slurry, the Sørensen *et al.* (2017) model estimates 27% and 10% mineralization of the organic N input in the first and second residual year, respectively. Based on NFRV from the present study, mineralization of residual organic N from pig slurry was somewhat higher at 35% in 2018 and 13% in 2019 (Table 5). The NFRV was similar for all liquid−solid mixtures from cattle slurry, while observed differences between liquid−solid mixtures from pig slurry could not be explained by the proportion of solid fraction.

Nitrogen mineralization and growing degree days

We found that net N mineralization rate of residual organic N from cattle slurries was close to zero during 0–2000 GDD. In the subsequent period (2000–5000 GDD), it averaged 0.0059%/GDD. For the pig slurries, the pattern was quite different with an initial fast mineralization rate for pig slurries at 0.0203%/GDD in the period 0–2000 GDD, followed by a lower rate in the subsequent period (2000–5000 GDD) with net N mineralization at 0.0105%/GDD. Bhogal *et al.* (2016) estimated net N mineralization from different manure types that were stripped of their ammonium content before being applied to soil. The mineralization of organic manure N was based on N uptake in grass and N leaching in a 5-year study on two sites. They also found that N mineralization could be divided in two distinct phases, but with a quite different pattern compared to our study. In the first phase until 2300 GDD degrees above 5°C, Bhogal *et al.* (2016) found that the cumulated mineralization as a percentage of organic N applied was proportional to thermal time with a mineralization rate of 0.0076%/GDD for cattle farmyard manure, cattle slurry and pig farmyard manure, while we found no significant net mineralization from cattle slurry in the period 0–2000 GDD. Bhogal *et al.* (2016) found net mineralization of 0.022%/GDD for pig slurry and layer manure in the first phase until 2300 GDD, which was comparable to the 0.0203%/GDD in the period 0–2000 GDD in our study. In the second phase after 2300 GDD (c. 1.5 years), Bhogal *et al.* (2016) found no differences between manure types and they reported a low rate of 0.0011%/GDD in one soil, whereas N mineralization could not be detected in the other soil. In contrast, we found significantly higher mineralization in the period 2000–5000 GDD for both manure types.

Conclusions

In the year of application, N associated with the solid fraction in slurry has the lowest plant availability. In the year after application (first year of residual effects), the NFRV related to total N application was higher from pig slurry mixtures than from cattle slurry mixtures.

In the first and second residual year, the net mineralization of residual organic manure N related to GDD was nearly constant in the period 2000–5000 GDD with an average mineralization rate of 0.0059%/GDD for cattle slurry mixtures and 0.0105%/GDD for pig slurry mixtures. The net N mineralization in the period 0–2000 GDD was more variable depending on the liquid-solid fraction ratio and was negligible from cattle slurry mixtures and high from pig slurry mixtures. When estimating the residual value of manures in the year following application, the different N release pattern, with a significantly faster release rate from fresh pig compared to stored cattle slurries, should be accounted for. However, the proportion of solid fraction from a given slurry type has no clear effect on N release related to total N applied and an estimation of residual N effect can be based on total N application for a given slurry type.

Acknowledgment. We wish to thank the technical staff at the Department of Agroecology, Aarhus University, Denmark, especially Margit Paulsen, for advice and assistance both in the field and lab.

Financial support. The research was funded partly by the Department of Agroecology, Aarhus University and by the Graduate School of Science and Technology at Arhus University.

Conflict of interest. The authors declare there are no conflicts of interest.

Ethical standards. Not applicable.

References

Bates D, Mächler M, Bolker B and Walker S (2015) Fitting linear mixed-effects models using {lme4}. *Journal of Statistical Software* **67**, 1–48.

Bhogal A, Williams JR, Nicholson FA, Chadwick DR, Chambers KH and Chambers BJ (2016) Mineralization of organic nitrogen from farm manure applications. *Soil Use and Management* **32**, 32–43.

Bosshard C, Sørensen P, Frossard E, Dubois D, Mäder P, Nanzer S and Oberson A (2009) Nitrogen use efficiency of 15 N-labelled sheep manure and mineral fertiliser applied to microplots in long-term organic and conventional cropping systems. *Nutrient Cycling in Agroecosystems* **83**, 271–287.

Chadwick DR, John F, Pain BF, Chambers BJ and Williams J (2000) Plant uptake of nitrogen from the organic nitrogen fraction of animal manures: a laboratory experiment. *Journal of Agricultural Science* **134**, 159–168.

Chalk P, Inácio C and Chen D (2020) Tracing the dynamics of animal excreta N in the soil-plant-atmosphere continuum using 15N enrichment. *Advances in Agronomy* **160**, 187–247.

Cusick PR, Kelling KA, Powell JM and Munoz GR (2006) Estimates of residual dairy manure nitrogen availability using various techniques. *Journal of Environmental Quality* **35**, 2170–2177.

Jensen B, Sørensen P, Thomsen IK, Jensen ES and Christensen BT (1999) Availability of nitrogen in l5N-labeled ruminant manure components. *Soil Science Society of America Journal* **63**, 416–423.

Karimi R, Akinremi W and Flaten D (2018) Nitrogen- or phosphorus-based pig manure application rates affect soil test phosphorus and phosphorus loss risk. *Nutrient Cycling in Agroecosystems* **111**, 217–230.

Klausner SD, Kanneganti VR and Bouldin DR (1994) An approach for estimating a decay series for organic nitrogen in animal manure. *Agronomy Journal* **86**, 897–903.

Li X, Sørensen P, Li F, Petersen SO and Olesen JE (2015) Quantifying biological nitrogen fixation of different catch crops, and residual effects of roots and tops on nitrogen uptake in barley using in-situ 15N labelling. *Plant and Soil* **395**, 273–287.

Peters K and Jensen LS (2011) Biochemical characteristics of solid fractions from animal slurry separation and their effects on C and N mineralisation in soil. *Biology and Fertility of Soils* **47**, 447–455.

Qian P and Schoenau JJ (2002) Availability of nitrogen in solid manure amendments with different C:N ratios. *Canadian Journal of Soil Science* **82**, 219–225.

R Core Team (2018) *R: A Language and Environment for Statistical Computing*. Vienna, Austria: R Foundation for Statistical Computing.

Reijs JW, Sonneveld MPW, Sørensen P, Schils RLM, Groot JCJ and Lantinga EA (2007) Effects of different diets on utilization of nitrogen from cattle slurry applied to grassland on a sandy soil in The Netherlands. *Agriculture, Ecosystems & Environment* **118**, 65–79.

Sommer SG and Hutchings NJ (2001) Ammonia emission from field applied manure and its reduction - invited paper. *European Journal of Agronomy* **15**, 1–15.

Sommer SG, Kjellerup V and Kristjansen O (1992) Determination of total ammonium nitrogen in Pig and cattle slurry: sample preparation and analysis. *Acta Agriculturae Scandinavica, Section B — Soil & Plant Science* **42**, 146–151.

Sørensen P (1998) Effects of storage time and straw content of cattle slurry on the mineralization of nitrogen and carbon in soil. *Biology and Fertility of Soils* **27**, 85–91.

Sørensen P and Amato M (2002) Remineralisation and residual effects of N after application of pig slurry to soil. *European Journal of Agronomy* **16**, 81–95.

Sørensen P and Thomsen IK (2005) Separation of Pig slurry and plant utilization and loss of nitrogen-15-labeled slurry nitrogen. *Soil Science Society of America Journal* **69**, 1644–1651.

Sørensen P, Weisbjerg MR and Lund P (2003) Dietary effects on the composition and plant utilization of nitrogen in dairy cattle manure. *The Journal of Agricultural Science* **141**, 79–91.

Sørensen P, Thomsen IK and Schröder JJ (2017) Empirical model for mineralisation of manure nitrogen in soil. *Soil Research* **55**, 500–505.

Sørensen P, Bechini L and Jensen LS (2019) Manure management in organic farming. In Köpke U (ed.), *Improving Organic Crop Cultivation*. Cambridge, UK: Burleigh Dodds Science Publishing, pp. 179–209.

Webb J, Sørensen P, Velthof G, Amon B, Pinto M, Rodhe L, Salomon E, Hutchings N, Burczyk P and Reid J (2013) An assessment of the variation of manure nitrogen efficiency throughout Europe and an appraisal of means to increase manure-N efficiency. In Sparks DL (ed.), *Advances in Agronomy*, Vol. **119**. San Diego, USA: Academic Press/Elsevier, pp. 371–442.