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ABSTRACT

Seven grassland experiments on sandy and clay soils were performed during a period of 4 years to estimate the nitrogen (N) fertilizer replacement value (NFRV) of concentrated liquid fractions of separated pig slurry (mineral concentrate: MC). The risk of nitrate leaching when applying MC was compared to when applying mineral fertilizers. Grassland yields in 2009–2012 fertilized with MC were compared with grassland fertilized with two mineral fertilizers: granulated calcium ammonium nitrate and liquid ammonium nitrate (LAN). The mineral fertilizers comprised 50% nitrate-N and 50% ammonium-N, and MC comprised 95–100% ammonium-N. Treatment application rates included zero N and three incremental rates of N fertilization. The liquid fertilizers were shallow injected (0–5 cm). The NFRV of MCs was 75% on sandy and 58% on clay soil with granulated ammonium nitrate as reference, and 89% on sandy and 92% on clay soil with LAN as reference. Risk of nitrate leaching after application of MC, measured in residual soil mineral N post-growing season and N in the upper groundwater in the following spring, was equal to that for mineral fertilizers.

Introduction

Animal manure comprises minerals that are used in agriculture as plant nutrients. However, the ratio of nutrients often does not match crop requirements. Nutrient combinations can be improved by processing animal manure to provide products containing (combinations of) nutrients in separate fractions. This processing of animal manure is expected to help to improve the efficiency of nutrient use. Moreover, many countries with high livestock population densities, similar to the Netherlands, often have a national balance surplus of phosphorus (P) in animal manure (MacDonald et al. 2011). This imbalance varies on individual farms. Transportation of P from one farm to another or abroad as unprocessed manure is costly as this involves large volumes of manure, containing up to 90% water. In addition, in the Netherlands, farmers have to pay to have animal manure removed because of the surplus supply and legislative restrictions on P fertilization in accordance with anticipated (average) removal at crop harvest. Transfer of animal manure also involves export of other component nutrients alongside P, including nitrogen (N) and potassium (K), while both N and K are imported in mineral fertilizer. Processed manure products that are, on the one hand, useful to farm management but, on the other hand, easily exported could decrease transport costs and increase the acceptance of animal manure usage by farmers. This could help reduce market pressure. Therefore, initiatives have been taken to separate excessive nutrients, especially P, from needed nutrients for arable and dairy farms, such as N and K. In the Netherlands, production of so-called mineral concentrate (MC) has been accomplished by a processing method involving the separation of manure into a solid and a liquid fraction followed by reversed osmosis (RO) to concentrate the liquid fraction and

decrease volume (Velthof et al. 2012). The resulting solid fraction comprises most of the P and organic N from the original material and is potentially exportable. MCs comprise almost solely ammonium N and K together with some dissolved nutrients and could be applied to farmlands within the Netherlands. However, MC is a new product for farms in the Netherlands. In order to utilize this product efficiently, it is essential to determine its N fertilizer replacement value (NFRV), on both arable land and grassland. Ammonium N is the most important component that determines the annual NFRV (De Boer 2008a; Schröder and Sørensen 2011). However, the NFRV of the ammonium in slurry is estimated but has never been measured separately, while it is common practice in the Netherlands to apply unprocessed animal manure mostly as slurry in which ammonium N and organic N are combined. Pig slurry comprises approximately 40% organic and 60% ammonium N, the ratio in cattle slurry is approximately 50:50. Considering MCs, Ehlert and Hoeksma (2011) hypothesized that the NFRV of MCs would be dependent on the amount of ammonia volatilization. They estimated that the NFRV would be about 94% without ammonia volatilization but would be reduced by ammonia volatilization to 76–90% on arable land and 67–81% on grassland using disc injection. This hypothesis was based on a theoretical approach. Therefore, experiments were performed to determine the NFRV of MCs in practice. Details of experiments on arable land have been published (Schröder et al. 2014). In the Netherlands, grassland field experiments were performed from 2009 to 2012. During these field experiments, N and dry matter (DM) yield were measured together with residual mineral N in the soil after the growing season and nitrate in the upper groundwater in order to determine whether or not the use of MC increases the risk of nitrate leaching (Schröder et al. 2010; Ten Berge et al. 2004). Therefore, the objectives of the field experiments in this study were:

- to determine the NFRV of MCs on grassland in sandy and clay soils, compared to mineral fertilizers.
- to determine the risks of nitrate leaching when applying MCs at comparable levels to mineral fertilizers.

Materials and methods

Location description, experimental design, and treatments

In the period from 2009 through 2012, seven grassland experiments were performed on permanent grassland. In 2009 and 2010, experiments were performed on both sandy soil, indicated as S09 and S10, and clay soil, indicated as C09 and C10. In 2011, one experiment was performed on a sandy soil, indicated as S11. In 2012, an experiment was performed on sandy soil with a relatively high groundwater table (79 cm below the surface in spring 2013), indicated as S12-w, and on sandy soil with a relatively low groundwater table (135 cm below the surface in spring 2013), indicated as S12-d. All experiments were performed on new fields each time on sand, and on new sections of a field on clay. The exact age of the swards was unknown, but they had been established at least more than 1 year previous to the experiments. All swards comprised primarily lolium perenne. Soil characteristics and coordinates of all seven sites are given in Table 1.

The experimental design was a randomized complete block design with two replicates—in S09, S10, S11, C09, and C10 and three replicates in S12-w and S12-d. Each year, the experimental treatments consisted of a control (zero N) and three incremental rates of nitrogen (N, Table 2) applied as (granulated) calcium ammonium nitrate (CAN), liquid ammonium nitrate (LAN), and MC. The applied MCs were from different producers and had slightly different mineral contents (Table 3). In S09, S10, S11, C09, and C10, the N application levels were combined with three other treatments: fertilization before one cut (first cut), before each of two cuts (first and second cuts), or before each of three cuts (first, second, and third cuts) (Table 4). This experimental design was earlier developed and applied by De Boer (2008b) in field research on point injection of liquid fertilizer with a spoke-wheel injector (2007–2009). In S12-w and S12-d, all fertilizers were applied before each of the three cuts (first, second, and third cuts). The expectation was that application before each of the three cuts would average out different application

Table 1. Soil characteristics in 0–10 cm of experimental sites and **location coordinates.**

	Soil type					
	Sand	Clay	Sand	Sand	Sand Low GT	Sand High GT
Sampling time	Spring 2009	Spring 2009*	Spring 2010	Spring 2011	Spring 2012	Spring 2012
Organic matter (%)	5.3	6.1	5.2	6.2	5.4	5.5
Total N (mg/100 g)	204	290	204	224	272	306
Soil N supply (kg N/ha/year)	140	130	140	140	160	170
P (mg P_2O5/100 g)	45	38	58	59	58	19
K (mg K_2O/100 g)	32	37	29	16	55	24
Mg (MgO, mg/kg)	198	358	237	259	250	174
pH—KCl	6,0	6,9	4,7	5,4	5,0	4,9
C/N ratio	Nd	Nd	12,8	13,9	10,0	9,0
Fraction <2 μm (%)	Nd	24	7.8	3.9	1.7	2.2
Coordinate	N52°	N52°	N52°	N52°	N52°	N52°

Nd: not determined; GT: groundwater table.
*Clay 2010 same location as 2009, other half of trial site, soil sample valid for 2009 and 2010.
P based on 0.1 N ammonium lactate/0.4 N acetic acid extractable P (P-AL-value) (Egnér, Riehm, and Domingo 1960), K based on 0.1 N HCl extractable K, Mg based on 0.5 N NaCl extractable Mg.

Table 2. Nitrogen fertilization with mineral fertilizers and mineral concentrates (kg N ha^{-1}) in experiments in 2009 to 2012.

			Cut			
Year	Fertilizer	N-level	1	2	3	Total
2009	Control*	0	0	0	0	0
2009	CAN/LAN	1	40	30	30	100
2009	CAN/LAN	2	80	60	60	200
2009	CAN/LAN	3	120	90	90	300
2009	MC	1	38	28	28	94
2009	MC	2	75	56	56	187
2009	MC	3	112	84	84	281
2010	Control*	0	0	0	0	0
2010	CAN	1	40	40	40	120
2010	CAN	2	80	80	80	240
2010	CAN	3	120	120	120	360
2010	LAN	1	61	46	46	154
2010	LAN	2	123	92	92	307
2010	LAN	3	184	139	139	461
2010	MC	1	40	31	31	101
2010	MC	2	80	61	61	202
2010	MC	3	120	91	91	303
2011	Control*	0	0	0	0	0
2011	CAN	1	40	40	40	120
2011	CAN	2	80	80	80	240
2011	CAN	3	120	120	120	360
2011	LAN	1	29	26	24	79
2011	LAN	2	59	52	47	158
2011	LAN	3	88	79	71	237
2011	MC	1	34	25	25	84
2011	MC	2	68	51	50	169
2011	MC	3	102	76	75	254
2012	Control*	0	0	0	0	0
2012	CAN	1	20	30	30	80
2012	CAN	2	40	60	60	160
2012	CAN	3	60	90	90	240
2012	LAN	1	34	27	24	85
2012	LAN	2	69	53	48	170
2012	LAN	3	103	80	73	256
2012	MC	1	38	27	28	93
2012	MC	2	77	54	57	189
2012	MC	3	111	81	86	278

CAN: calcium ammonium nitrate, LAN: liquid ammonium nitrate, MC: mineral concentrate.
*Control: with and without slits in the soil surface.

Table 3. Mean contents in g kg^{-1} of mineral concentrates, sampled from application tank before and after application.

Year	Mineral concentrate	Total N	NH$_4$-N	pH	P	K	S
2009	A	6.8	6.3	Nd	0.21	8.01	0.25
	C	9.0	7.8	Nd	0.34	8.11	0.41
	D	5.5	4.8	Nd	0.10	6.19	0.25
2010	A	6.2	6.1	8.1	0.10	6.43	0.25
	B	6.8	6.4	7.8	0.02	7.10	0.41
	E	4.5	3.9	7.9	0.09	5.89	0.25
2011	B	9.3	8.9	8.1	0.03	8.4	Nd
2012	B	7.5	7.1	Nd	0.02	6.8	Nd

Nd: not determined; A to E: code for producer of mineral concentrate.

Table 4. Schedule of application of mineral concentrate and liquid ammonium nitrate and precipitation levels on application day, from nearest weather station (Source: http://www.knmi.nl/klimatologie/monv/reeksen/).

Year	Site	Application date	Precipitation, mm day^{-1}	Site	Application date	Precipitation, mm day^{-1}
2009	Sand	23 March	0.8	Clay	24 March	2.4
		6 May	8.1		8 May	0.0
		10 June	1.3		11 June	16.6
2010	Sand	31 March	0.7	Clay	30 March	0.3
		10 May	0.0		11 May	1.3
		8 June	0.0		9 June	5.0
2011	Sand	1 April	5.3			
		4 May	0.0			
		10 June	0.0			
2012	Dry/wet sand	26 March	0.0			
		15 May	0.3			
		13/15 June	0.0/0.4			

NB: Granulated fertilizers (calcium ammonium nitrate, superphosphate, and kornkali) were applied maximally 1 day apart.

circumstances and growing conditions within each year. Application before one and two cuts provided a possibility to distinguish the efficacy of the N fertilization between the individual cuts. In S09, S10, C09, and C10, MCs from three different producers were applied and in S11, S12-w, and S12-d, with MC from a single producer. The MCs were applied with a prototype application machine that cut slits in the sod with a coulter. The machine will be further described in the next section. Controls (zero N) were assigned to either granulated or liquid fertilizer. Control treatment areas were subjected to passes with the liquid fertilizer application machine simulating fertilizer application without actual application. This was performed in an attempt to simulate any effects attributable to mechanical damage to the grass roots and structural damage due to soil compaction by the application machine. On all sites, two control plots per replication for the granulated fertilizers were laid out. The number of control plots per replication per number of fertilizations for the liquid fertilizers was three on experiments S09, S10, C09, and C10, resulting in nine control plots, and two on S11, S12-w, and S12-d, resulting in six control plots. In S10 and C10, extra plots were fertilized for three cuts with granulated CAN and subjected to three passes with the application machine for liquid fertilizer to determine whether or not the use of the application machine interacted with N fertilization level. The numbers of plots for S09 and C09 was: (11 control + 5 types of fertilizer × 3 N levels × 3 numbers of fertilizations) × 2 replications = 112; for S10 and C10: number of fields in 2009 and 1 + 6 extra plots CAN with slits = 118; for experiment S11: (8 control + 3 types of fertilizer × 3 N levels × 3 numbers of fertilizations) × 2 replications = 70; for experiment S12-w and S12-d: (4 control + 3 types of fertilizer × 3 N levels) × 3 replications × 2 sites = 78.

Management of the experiment

In S09, S10, S11, C09, and C10, the plots were 3 m × 10 m in dimension. In S12-d and S12-w, the plots were increased to 6 m × 10 m because nitrate was measured in groundwater in the following spring,

requiring larger plots. After the first cut, the plots were fertilized within 2 days after harvesting. The CAN, P, and K were applied with an accurate granulate spreader used for experimental fields or by hand by qualified experimental farm staff. In S12-w and S12-d, the plots were fertilized in two halves in opposite directions in order to ensure accuracy of spread.

A prototype machine developed at the experimental farm of Applied Plant Research (Wageningen University and Research Centre) was used to apply the liquid fertilizers. This prototype machine was constructed on a frame with a 1000 l storage tank and had a pump system similar to a conventional crop sprayer. Outflow rate was regulated accurately by pump pressure, size of outflow aperture, and the groundspeed of a calibrated tractor. The injection unit was mounted on a frame with 18 coulters with a total width of 3 m coinciding to the width of the experimental plots. Outflow rate was calibrated daily prior to application by pumping water through the machine, collecting the outflow in containers, and measuring the amount after a set period of time. This machine was developed because it was not possible to apply the planned amounts of MC with a normal slurry injector due to low application rates. The machine cut through the sod with coulters and deposited the liquid fertilizers into the slits. For application on grassland, the coulter was set at 5 cm below the surface with a wheel. The result was visually comparable with an adjusted disc injector.

The MCs contained a relatively high concentration of K (7.8%) and a low concentration of P (0.21%) (Table 3). All plots received a P and K fertilization, equal to the largest P and K fertilization rate that was applied with MC as superphosphate (20% phosphorus pentoxide (P_2O5)) and kornkali (40% potassium oxide (K_2O)) using the same spreader as CAN or by hand. This indicates that on the lower N fertilization levels, an additional dressing was given. All plots received more sulfur (S) with MC and/or superphosphate (11% S) and kornkali (5% S) than recommended; therefore, no separate S fertilization was applied. The LAN was diluted to a concentration that was comparable to the MC concentration. The liquid fertilizers and MCs were sampled from the tank before and after fertilization of all plots at each site.

During the growing season, five cuts were harvested from all plots on the same day per site. The first cut was estimated to provide a yield harvesting 3500 kg DM ha^{-1} on the fastest growing plot. Subsequent cuts were aimed to provide 2500 kg DM ha^{-1} or after 5–6 weeks, depending on the rate of growth. The time of harvest was estimated visually. Grass was harvested from an area of 1.5 m × ca. 8 m (measured afterward) at 5 cm above the surface level with a Haldrup forage harvester.

Sampling and chemical analysis

Herbage fresh weight was determined and sampled from every plot. Herbage samples were dried at 70 °C for 48 h for analysis of DM content. Total N contents of grass were determined following digestion with a mixture of sulfuric acid, salicylic acid, hydrogen peroxide, and selenium (1984; Novozamsky et al. 1983). The N concentrations in the digests were measured by means of the indophenol blue method (Novozamsky et al. 1974). In order to determine the mineral soil-N content, soil samples were taken at the end of the growing season, within 14 days after the last harvest. Soil mineral N was analyzed in the soil layers 0–30, 30–60, and 60–90 cm below the surface, in a mixed sample of 10 sample points per plot. Only those plots that had been fertilized for three cuts were sampled because this is where the largest differences were expected between treatments. In 2009, samples were taken from the site on sandy soil; after 2009, all experimental sites were sampled.

In spring 2013, between 18 and 27 March, before the start of the next growing season, S12-w and S12-d were sampled and analyzed for nitrate in the upper layer of groundwater to measure the effect of the treatments in 2012 on risk of nitrate leaching in the following years. Five holes per plot were drilled using an Edelman drill, approximately 20 cm below the local groundwater table. A porous cup (filter holes 0.45 μm Φ) was used to sample at least 50 ml groundwater per drilling. All individual samples (five per plot) were analyzed for nitrate-N (N-NO$_3$), ammonium-N (N-NH$_4$), and total N (N$_{total}$).

Statistical analyses and calculation of NFRV

DM and N yields from each cut were summed per plot to determine annual yields. Differences between treatments in annual DM and N yields were statistically analyzed with a linear model composing a fixed and random component using restricted maximum likelihood (ReML) prediction modeling (Harville 1977) provided by the GENSTAT package (VSN International, Hemel Hemstead, UK). The fixed component comprised the experimental treatments as explanatory variables and the random component comprised random effects.

These "fixed" factors included the actual N fertilization, site, fertilizer type, year, and number of fertilized cuts. All factors and their interactions were included in the analysis, and all nonsignificant interactions ($P < 0.05$) were deleted from the model step by step. The structure of the random component of the statistical analysis comprised the factor "site × replicate × year." Inclusion of this interaction implies that data from a site, year, and replicate are interdependent. The number of observations resulted in enough degrees of freedom for the error term, in spite of only two replicates in 2009, 2010, and 2011.

In general, the relationship between N fertilization and grass yield was not considered to be linear but is curvilinear and approaches a maximum level (Mengel and Kirkby 2001; Vellinga and Andre 1999) since the yield increases more slowly at higher N application rates due to the law of diminishing returns. When considering a relatively small range of N fertilization rates, the curve is not necessarily relevant and the relationship can be described as (approaching) linearity. This was analyzed by adding a quadratic function (N fertilization^2) to the model. Therefore, the full starting model was:

$$\text{Yield (DM or N)} = \text{Constant}_{\text{soil type, slits, number of fertilizations}} + \beta 1_{\text{soiltype}} \times \text{N fertilization} + \beta 2_{\text{fertilizer type}} \times \text{N fertilization} + \beta 3_{\text{number of fertilizations}} \times \text{N fertilization} + \beta 4_{\text{fertilizer type, soiltype}} \times \text{N fertilization} + \beta 5_{\text{fertilizer type, soiltype, number of fertilizations}} \times \text{N fertilization} + \beta 6_{\text{soiltype}} \times \text{N fertilization}^2 + \varepsilon_{\text{site} \times \text{replicate} \times \text{year}}$$

(1)

where Constant is the intercept, N fertilization is N application rate (in kg N ha^{-1}), βs are coefficients, specific for soil type, fertilizer type, and/or number of N fertilizations. In the constant (intercept), the factors "slits" and "number of fertilizations" were included in the first full model because they could potentially influence the yield at 0N (intercept). Slits in the grass could have an effect on yield, and number of fertilizations corresponds with the number of times that slits are drawn in the grass.

The slope of the curve predicting the DM yield represents the apparent N efficiency (ANE) and that of the N yield represents the apparent N recovery (ANR) (Prins 1984; Vellinga and Andre 1999).

Expressed in formulae as:

$$\text{ANE at level X} = ((\text{DM yield at N level X}) - (\text{DM yield at N level 0}))/\text{kg N fertilization level X} \qquad (2)$$

$$\text{ANR at level X} = ((\text{N yield at N level X}) - (\text{N yield at N level 0}))/\text{kg N fertilization level X} \qquad (3)$$

The NFRV is the factor that N from (organic) fertilizer has to be multiplied by, to provide a response in relation to a reference fertilizer (Petersen 2003). The NFRV can be calculated by using the DM yield, (ANE), or N yield (ANR). The N yield was considered to provide a more reliable indicator of plant available N for each fertilizer type. Moreover, N contained in crude protein is also a valuable component of grass, which is a valuable fodder used by dairy farmers. An estimate of NFRV based on N yield will therefore provide a more suitable prediction for grassland than the one based on DM yield. Therefore, NFRV estimates for types of fertilizer were calculated by dividing the ANRs of the fertilizer type and the reference fertilizer (Schröder, Uenk, and Hilhorst 2007):

$$\text{N fertilizer value fertilizer type Y} = (\text{ANR fertilizer type Y})/(\text{ANR reference fertilizer}) \qquad (4)$$

The NFRVs were calculated with both CAN and LAN as reference fertilizer.

Mineral soil N and N in groundwater were also analyzed using ReML modeling. The starting model was:

$$Y = \text{Constant}_{\text{soil type} \times \text{year}} + \beta 1_{\text{site}} \times \text{N fertilization} + \beta 2_{\text{fertilizer type}} \times \text{N fertilization} + \beta 3_{\text{fertilizer type} \times \text{site}}$$

$$\times \text{N fertilization} + \varepsilon_{\text{site} \times \text{replicate} \times \text{year}} \tag{5}$$

where Y is mineral N in soil or N in groundwater, N fertilization is N application rate (in kg N ha^{-1}), βs are coefficients, and specific for site and/or fertilizer type, ε is residual variance. The mineral N was measured in mg N l^{-1} soil and was calculated to kg N ha^{-1} = mg N l^{-1} × (sample depth in cm × 10^{-1}).

Results

Yield and NFRV

DM and N yields increased with increasing N fertilization rates at all locations, according to year, and fertilizer type (Figures 1 and 2). In the statistical analysis of the control plots (no N fertilizer), slits had no effect on N yield or DM yield (results not shown). In addition, the N and DM yields for CAN and CAN + slits did not differ in 2010, indicating that the slits did not interact with the effect of N fertilization level. Consequently, only fertilizer type and interaction with N fertilization were used in the linear model. The consequence of this model was that the influence of fertilizer type was zero when N fertilization was zero; therefore, the same intercept was used for all fertilizer types.

In the analysis of the DM yield, the factors N fertilization and N fertilization^2 were significant (Table 5), indicating that the increase of DM yield diminished as N application rates increased. The two-way interactions (site × N fertilization) and (N fertilization × number of fertilized cuts) and the three-way interaction (site × fertilizer type × N fertilization) all had an effect on DM yield (Table 5). In the analysis of the N yield, the factor N fertilization and the three-way interaction (soil type × fertilizer type × N fertilization) had an effect (Table 5). The differences between the efficacy (=ANR) of CAN, LAN, and MC are expressed in this last interaction.

Determination of the NFRV of the MCs, based on CAN and LAN, was calibrated with data based on the model used for statistical analysis of the N yield. In order to obtain an impression of the variation between years, overall NFRVs were calculated and per year for soil type. For calibration per year, the factors "year" and "site" are transferred from the random to the fixed component in the model. The resulting model for N yield per year per site is:

$$\text{N yield}_{\text{year} \times \text{site}} = \text{Constant}_{\text{year} \times \text{site}} + \beta_{\text{year} \times \text{fertilizer type} \times \text{site}} \times \text{N fertilization} + \varepsilon_{\text{replicate}} \tag{6}$$

where N yield is in kg N ha^{-1} for specific year and site, Constant (in kg N ha^{-1}) is the intercept for specific year and site, β is a coefficient depending on year, fertilizer type, and site for N fertilization and equals the ANR, N fertilization is N application rate (in kg N ha^{-1}), and ε is residual variance. In Figure 2, the outcomes of the linear model and 95% confidence interval of the slopes are given. The slopes were significantly different if the confidence intervals did not overlap. The slopes were significantly higher for CAN application than MC application in most years, except for S11 and S12-d where no difference was found. The slopes for LAN compared to MC were higher in experiments S09, C09, S11, S12-w, and S12-d and lower in S10 and C10. However, the differences were not significant, except in C10. The slopes for CAN compared to LAN were significantly higher in S09, S10, C09, and C10 and not significantly different in S11, S12-w, and S12-d.

Using the model results for CAN, LAN, and MC, estimates for the ANRs (Equation 3), equal to the slopes of the linear models, were used to calculate the NFRVs (Eq. (4)) (Table 6). In general, the NFRV for MC with CAN as reference was 75% on sandy and 58% on clay soil. However, there was a large between-year variance. On sandy soil, the lowest NFRV for MC was 61% in 2009 and the highest was 82% on dry sand in 2012. Only results from two experimental years were available for clay and the NFRVs were 44% (2009) and 67% (2010). The lower NFRV on clay soil was attributable to a relatively high ANR value for CAN. ANR values for MC on clay were within the same range as the ANR for MC on sandy soil. However, the high ANRs for CAN are considered normal for this specific clay site (Schils and Snijders 2004).
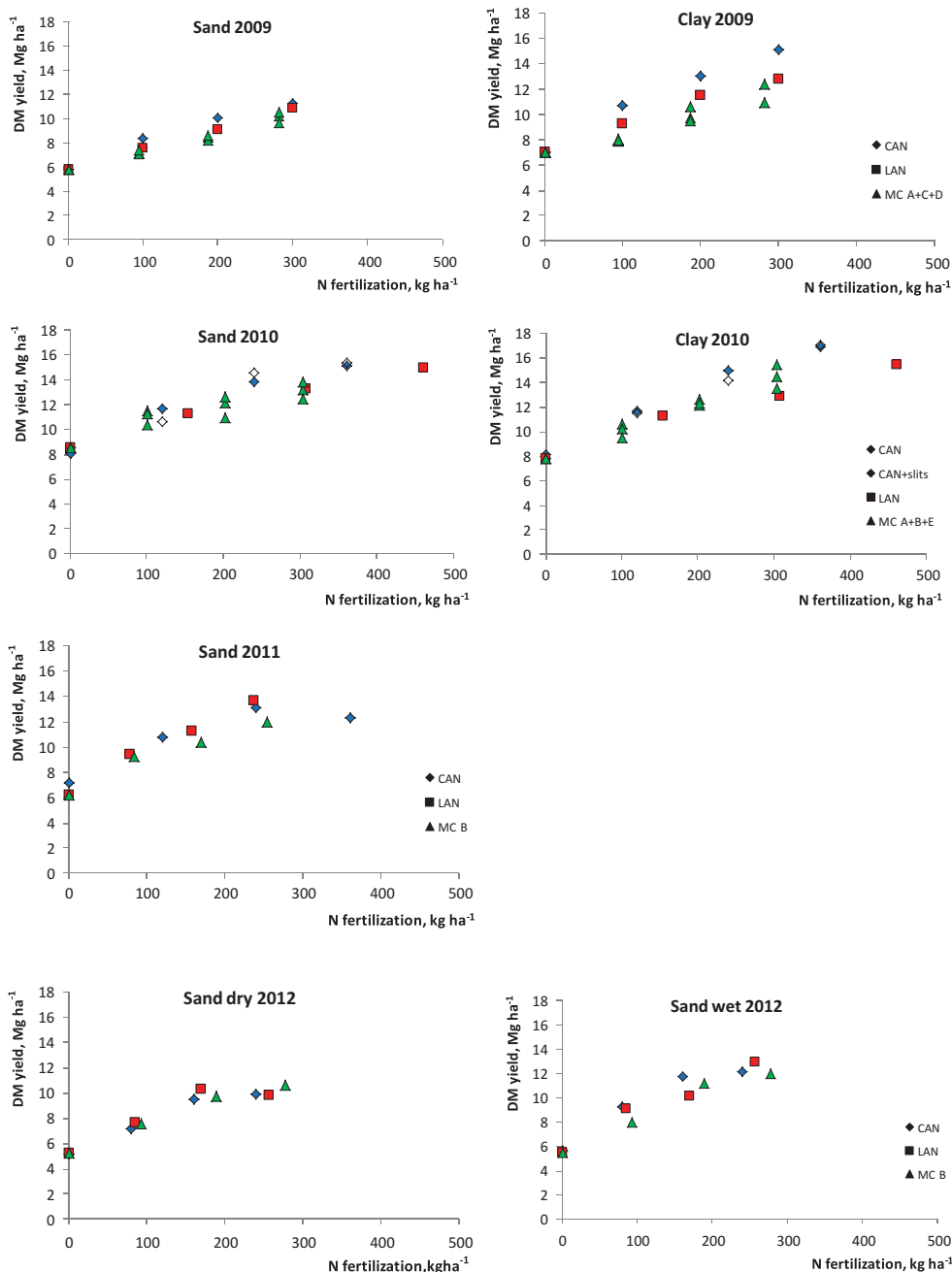
Figure 1. Dry matter yield (Mg ha^{-1}) at incremental N fertilizations with calcium ammonium nitrate (CAN), CAN with slits (CAN +slits), liquid ammonium nitrate (LAN), and mineral concentrates (MC: A, B, C, D, E: code for producer of MC), on sand and clay, from 2009 to 2012, mean of plots that are fertilizes before three cuts.

Mineral N in soil and nitrate in upper groundwater

After the growing season, the values of mineral N at 0–90 cm below the surface showed no consistent or systematic influence from fertilizer type or N fertilization level (Figure 3). Differences between years were large. The statistical analysis showed high standard deviations within
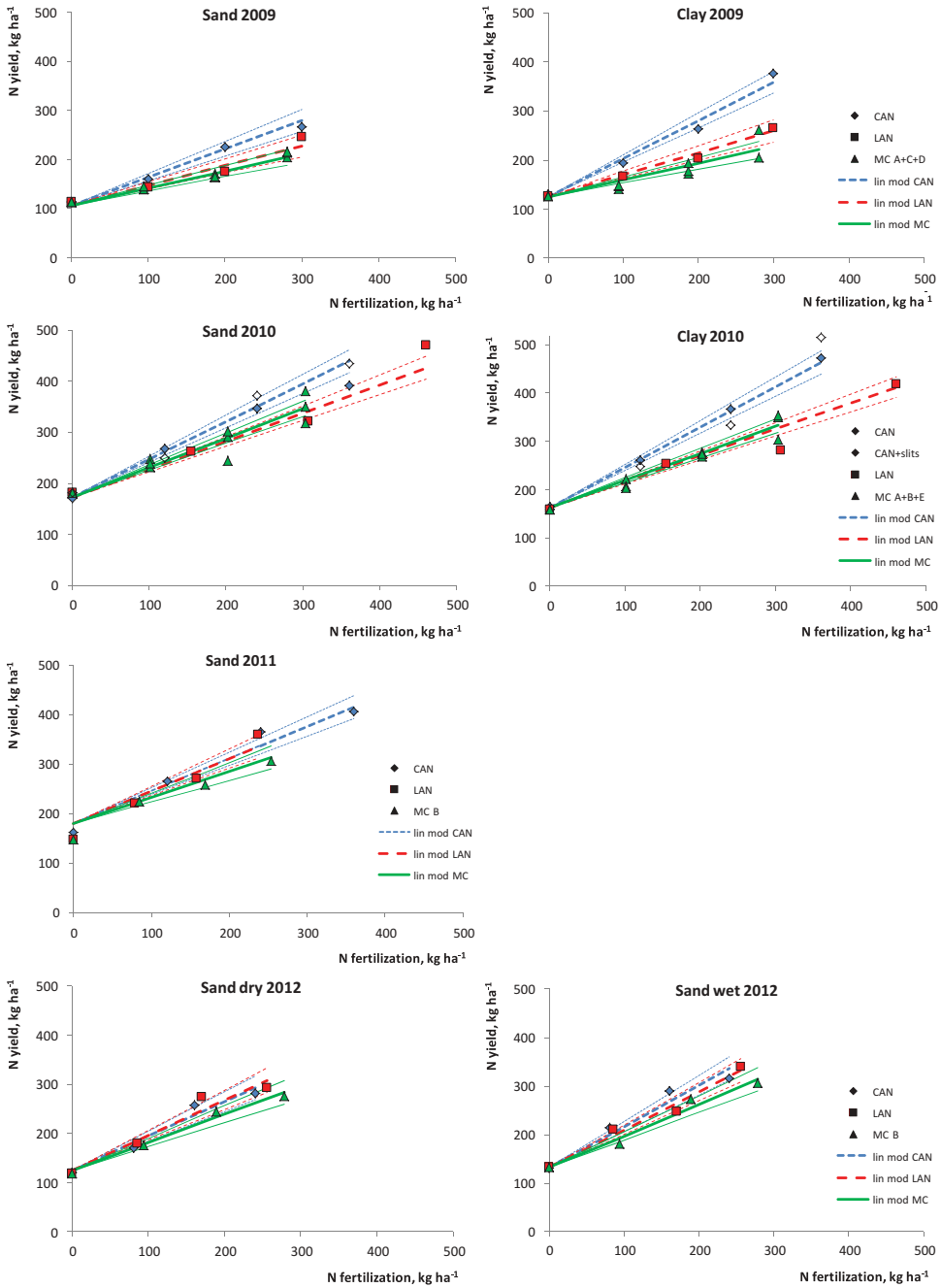
Figure 2. Nitrogen yield (kg ha⁻¹) at incremental N fertilizations with calcium ammonium nitrate (CAN), CAN with slits (CAN+slits), liquid ammonium nitrate (LAN), and mineral concentrates (MC: A, B, C, D, E: code for producer of MC), on sand and clay, from 2009 to 2012, mean of plots that are fertilized before three cuts; linear model (lin mod); 95% confidence interval of gradient (estimate plus and minus least significant difference; thin lines in corresponding color).

sites and years of experiments. Only site × year had a significant effect. Total N in the upper groundwater in the experimental fields showed no influence from N fertilization level (2012) or fertilizer type in the spring of 2013 (Figure 4).

Table 5. Probability levels for factors (and interactions) influencing dry matter and nitrogen yield (based on statistical analysis with reduced maximum likelihood).

	Probability (P < 0.05)	
Fixed term	DM yield	N yield
Soil type	0.327 (n.s.)	0.813 (n.s.)
N fertilization	<0.001	<0.001
Soil type × N fertilization	0.014	n.s.
N fertilization × number of fertilizations	<0.001	n.s.
Soil type × fertilizer type × N fertilization	<0.001	<0.001
Nfertilization^2	<0.001	n.s.

n.s.: not significant.

Table 6. Apparent nitrogen recovery (ANR, kg N/kg N) of three fertilizer types and nitrogen fertilizer replacement value (NFRV), on sandy and clay soil sites in 2009 to 2012 (nitrogen yield compared with two reference fertilizers).

					NFRV, %			
		ANR, kg N kg^{-1} N			Reference: CAN		Reference: LAN	
		CAN	LAN	MC	LAN	MC	CAN	MC
2009	Sand	0.58 (±0.07)*	0.41 (±0.07)	0.35 (±0.06)	70	60	143	86
	Clay	0.78 (±0.07)	0.45 (±0.07)	0.34 (±0.06)	58	44	174	76
2010	Sand	0.74 (±0.06)	0.55 (±0.05)	0.58 (±0.05)	74	78	135	105
	Clay	0.84 (±0.07)	0.54 (±0.05)	0.56 (±0.05)	65	67	155	104
2011	Sand	0.65 (±0.07)	0.65 (±0.10)	0.52 (±0.09)	100	80	100	80
2012	Dry sand	0.70 (±0.10)	0.71 (±0.10)	0.57 (±0.09)	102	82	98	80
	Wet sand	0.85 (±0.10)	0.78 (±0.10)	0.65 (±0.09)	92	77	108	84
Over	Sand	0.69 (±0.04)	0.59 (±0.04)	0.52 (±0.04)	76	85	117	89
all	Clay	0.82 (±0.06)	0.52 (±0.05)	0.48 (±0.05)	59	63	158	93

CAN: calcium ammonium nitrate; LAN: liquid ammonium nitrate; MC: mineral concentrate.
*Means and least significant difference (in brackets, P ≤ 0.05).
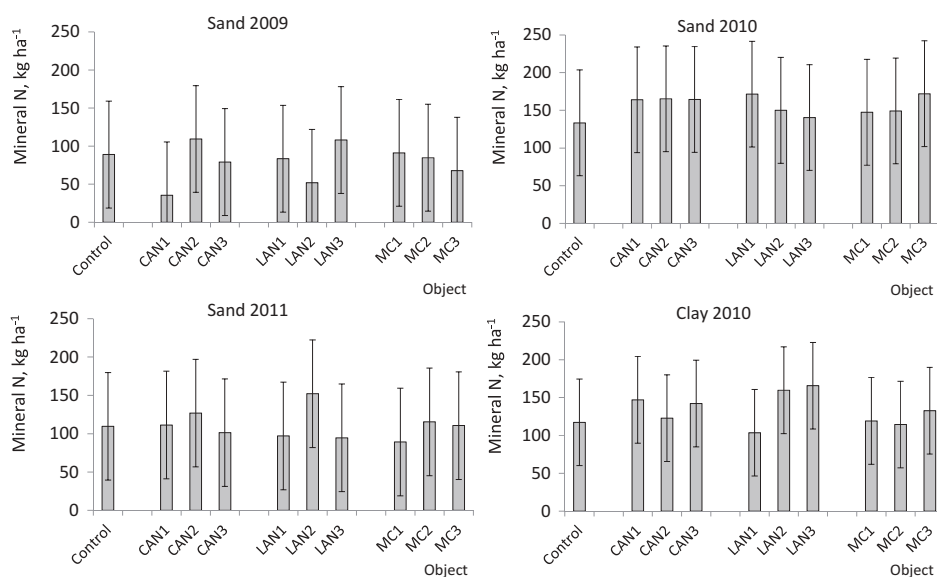
Figure 3. Soil mineral nitrogen (N) 0–90 cm below the surface in sandy soil in 2009 to 2011 and clay in 2010, at the end of growing season; No N fertilization (Control), fertilization with calcium ammonium nitrate (CAN), liquid ammonium nitrate (LAN), and mineral concentrates (MC); and three levels of N fertilization (1 to 3); Error bar: least significant difference (P < 0.05).
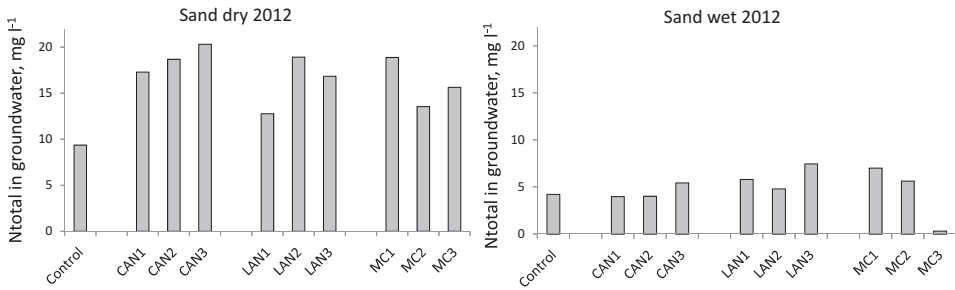
Figure 4. Total nitrogen (N) in upper groundwater 20 cm below groundwater level in dry and wet sandy soil in spring 2013, after experiment in 2012; Dry: average groundwater table 135 cm, wet: average groundwater table 79 cm, below surface spring 2013; No N fertilization (Control), fertilization with calcium ammonium nitrate (CAN), liquid ammonium nitrate (LAN) and mineral concentrates (MC); and three levels of N fertilization (1 to 3); MC3 on wet sand: below detection limit.

Discussion

Grassland yields in N and DM responded to N application using all fertilizer types. However, responses of MC and LAN were lower than expected (Ehlert and Hoeksma 2011). It is not clear why the responses of DM and N yield were lower to MC and LAN than to CAN in most years. It is, however, not uncommon that liquid fertilizers, applied with shallow injection or point injection on grassland, have a lower response than CAN (De Boer 2009). The cause or mechanism for this difference is not known.

A potential source of variation could have been the use of the experimental machine for application of LAN and MC. The application rate was dependent on the outflow rate and the groundspeed of the tractor. The outflow rate per time unit was measured several times and the groundspeed of the calibrated tractor was adjusted to provide the required dosage. A possible inaccuracy could have been caused by wheel slip. Wheel slip would cause a higher application rate than calculated and would consequently result in an overestimation of the NFRVs for both LAN and MC. However, it is considered that wheel slip did not occur to a high degree, based on visual observations and soil/weather conditions. This was confirmed by the residuals of the MCs after application. Besides, the calculated NFRV in the experiment was lower than expected.

The coulters of the application machine cut into the sod of the grass. As shown in the results, this had no effect on yield. In an earlier experiment, the cutting effect of injection at 20 cm below the surface in grass resulted in a negative effect on the yield of grassland in the harvest directly after cutting but was compensated in subsequent harvests (Schils 1992).

Other possible sources of variation might be higher accumulation or losses of N when applying liquid fertilizers compared to CAN. Temporary accumulation seems unlikely since almost no residual effect of N applied was found by MC and LAN after the previous fertilization in the growing season which comprised at least two cuts for all objects (data not shown). This would seem to indicate that N not taken up from LAN and MC was not available in the soil after harvest. The observation that N concentration in groundwater was comparable for all fertilizer types confirms this. An incubation experiment by Ehlert, Nelemans, and Velthof (2012) during 56 weeks suggested that adding MCs did not affect immobilization or mineralization of N.

Possibly, gaseous losses of N play a significant role. Some arguments point in the direction of ammonia volatilization. The ammonia volatilization of slurry at shallow injection is estimated at 6% of the N in ammonium form on average in earlier research (Huijsmans, Hol, and Hendriks 2001). However, MCs, compared to slurry, comprise high ammonia concentrations with a high pH, about 8 (Table 3) and therefore are expected to be susceptible to ammonia losses during application. In addition to that, the NFRV in clay was lower than in the sandy soil during 2009 and 2010. Clay has a higher pH (Table 1) and could be responsible for higher ammonia emission levels. A high ammonia volatilization potential was also measured in controlled experiments with MC (Velthof et al. 2012). However, there

are other arguments opposed to ammonia volatilization as the cause of the low NFRV for MC: The N in LAN is not expected to be lost through ammonium volatilization as easily as in MC. LAN is more acidic (pH 4.0–6.0), and only half of the N is in the ammonia form, the other half is in the nitrate form. Ammonia volatilization could therefore explain the difference (approximately 10%) in ANR between LAN and MC but not the difference between LAN and CAN. Besides, the liquid fertilizers MC and LAN infiltrate the soil faster than slurry (visual observation, not quantified). Faster infiltration will decrease the risk of ammonia volatilization compared to a slower infiltration as with slurry (personal communication Jan Huijsmans). In addition to that, on many application days, especially before the first cuts in 2009 and in 2010 (Table 4), the weather was cloudy and rainy during application. This makes it unlikely that ammonia emission with MC in the experiments was higher than the earlier mentioned average of 6% during shallow injection with slurry (Huijsmans, Hol, and Hendriks 2001).

Gaseous loss through denitrification might also be a cause for a low NFRV of MC. In an incubation experiment, denitrification was 1.5 times higher when MC was applied than when pig slurry was applied, both incorporated in the soil (Velthof and Hummelink 2011). Denitrification after application of pig slurry is, however, in the order of magnitude of 1% of total N. Even a double loss through denitrification would not explain the relatively low NFRV of MCs that was found in the experiments.

In general, the relatively low NFRV of MC found on grassland in this experiment could not be explained. Gaseous losses during and after the application of MC could not be ruled out.

Conclusions

Overall, the NFRV of MCs with granulated ammonium nitrate as reference was 75% on sandy and 58% on clay soil. On sandy soil, this varied between years and sites from 61% to 82% and on clay from 44% to 67%.

In general, the NFRV of MCs in sandy soil was 89% and 92% in clay in comparison to LAN. In sandy soil, this varied between years and sites from 80% to 105% and in clay from 76% to 104%.

Quantification of gaseous losses could be necessary to explain the low NFRV of MCs and could therefore be the focus of future studies.

The risk of nitrate leaching during application of MCs, measured in residual mineral N after the growing season and in N in the upper groundwater in the following spring, was equal to the risk of nitrate leaching for the mineral fertilizers CAN and LAN.

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