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## Nitrate leaching from liquid cattle manure compared to synthetic fertilizer applied to grassland or silage maize in the Netherlands

Herman de Boer



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# Foreword

Nitrate leaching from dairy farming can contribute to the pollution of ground- and surface water. In Dutch dairy farming, grassland and silage maize are the predominantly grown crops and both are fertilized with a combination of liquid dairy cattle manure and synthetic fertilizer calcium ammonium nitrate. The use of both fertilizer types is restricted to prevent excessive nitrate leaching. However, it is not clear if or what differences exist in the relative contribution of these fertilizer types to nitrate leaching. The results of this literature analysis contribute to the understanding of the processes and management practices that determine nitrate leaching potential from both fertilizer types applied to grassland and silage maize and indicate the differences in leaching that can be expected.

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# Summary

In the Netherlands, liquid dairy cattle manure (LCM), a mixture of cow urine and faeces, currently has the reputation of being a relatively environmentally unfriendly nitrogen (N) fertilizer when compared to the synthetic fertilizer calcium ammonium nitrate (CAN). In discussions on the effectiveness of current manure legislation, it is proposed that the manure N application rate should be reduced and the reduction in plant-available N be replaced by an equal amount of N from CAN, as a strategy to remain below the EU nitrate concentration limits in ground- and surface water. In contrast to LCM, CAN is reputed to be a highly efficient N fertilizer with relatively low nitrate leaching. However, there is evidence to suggest that the N use efficiency of CAN can be relatively low on sandy soils and that relatively high nitrate leaching losses can be realized shortly after application. The objective of this study was to analyse differences in the risk and level of nitrate leaching from (injected) LCM and CAN, at the same level of crop N uptake, when applied to permanent grassland and silage maize. Also, three specific questions were investigated: 1) Is nitrate leaching from LCM in general higher than from CAN, when compared at the same level of N uptake? 2) Will the recent reduction in the manure N derogation limit from 250 to 230 kg total N ha<sup>-1</sup> on leaching-sensitive sandy soils, and replacement of the difference by CAN on NFRV-basis, result in a lower level of nitrate leaching?; and 3) Would a general reduction in the manure N derogation limit from 250 to 170 kg total N ha<sup>-1</sup>, and replacement of the difference with CAN on NFRV-basis, result in lower nitrate leaching from Dutch dairy farms?

The results of this study show that there are some fundamental differences in short- and longer term nitrate leaching risk between LCM and CAN due to a difference in N formulation. In CAN, half of the N is present as ammonium and the other half as nitrate. In LCM, half of the N is also present as ammonium but the other half as organic N. During the growing season, nitrate is at increased risk of direct leaching by preferential flow through soil macro pores, following a period of prolonged or heavy rainfall. As half of the N in CAN is already present as nitrate, this nitrate is at immediate risk of being leached after application. With LCM, however, organic N has to be converted to ammonium, and from ammonium into nitrate, before leaching as nitrate can occur. Both conversions can take considerable time, during which nitrate accumulation is countered by plant N uptake. As plant uptake reduces the average nitrate concentration in soil, the nitrate leaching risk during the growing season can be smaller for LCM than CAN when applied to crops with ongoing N uptake during the growing season, such as grass.

It is unclear from current evidence whether the potential in-season advantage of LCM is offset by the increased (post-season) leaching risk arising from mineralisation of the organic N pool, a pool that increases over the years under repeated LCM application. Such offset is likely to occur under maize (as maize N uptake has declined or ceased during mid-summer, when soil N mineralization is active) and less likely under grassland (with its prolonged N uptake throughout the growing season, during the period with most active N mineralization)

In experimental studies and their interpretation, the contribution of nitrate leaching during the growing season is rarely considered. Consequently, (direct) nitrate leaching risk from CAN appears underestimated relative to LCM. Nitrate leaching risk increases when inorganic N is applied or becomes available at rates higher than necessary for optimum growth. Because drought reduces plant N uptake, this can also result in a relative oversupply of inorganic N, accumulation of nitrate in soil and increased nitrate leaching when leaching loss pathways become active. As organic N in LCM is only slowly converted into nitrate, and the conversion rate is even more reduced during drought, the difference in leaching may increase due to drought, which occurs more frequently on drought-sensitive (sandy) soils.

For cut grassland, the available evidence suggests that replacement of CAN by LCM decreases short-term nitrate leaching, at the same level of N uptake. The level of leaching from LCM is low and 400 kg N ha<sup>-1</sup> year<sup>-1</sup> or more can be applied without increased leaching risk in the short term, provided good agronomic practices are applied. However, an increase in the amount and mineralization of soil

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organic N over the years (until a steady state is reached) necessitates a reduction of the supplementary CAN application over the years, to prevent a relative oversupply of inorganic N and an increased nitrate leaching risk. There is a lack of data from long-term grassland experiments with separate and repeated application of (injected) LCM or CAN, and combinations of both fertilizers, to be used for a full, integrated evaluation of nitrate leaching potential of these individual fertilizers in the long term.

Grassland grazing instead of cutting can strongly increase nitrate leaching risk, as the N in urine and faeces is not evenly spread over the field (as with LCM), but randomly deposited in patches. Especially under urine patches, the inorganic N concentration is on average higher than can be absorbed by the affected grass during the remainder of the growing season, leaving the surplus at risk of being leached. Therefore, managing grazing intensity will be more effective to decrease nitrate leaching than a reduction in LCM or CAN application.

Maize has a short period with increased N uptake during the growing season, which lasts an estimated 4 to 6 weeks. Nitrogen uptake declines afterwards and ceases mid-July to mid-August. The inorganic N present in soil and mineralizing after, during the period with declining or absent crop N uptake, is prone to leaching. As a result, maize has a low N use efficiency, especially relative to cut grassland. When maize is grown in rotation with grassland, its low N use efficiency easily results in an oversupply of inorganic N and increased nitrate leaching from the rotation, especially in the first year, due to the mineralization flush after grassland destruction. A high level of LCM application during the grassland phase can further increase nitrate leaching risk during the arable/maize phase, as part of the applied organic N mineralizes after the cessation of maize N uptake. A relatively high level of LCM application to maize, replacing CAN on a NFRV-basis in the first year, therefore likely increases nitrate leaching risk in the longer term, although management practices can have a larger effect on potential nitrate leaching after maize than site conditions or previous fertilization history. There is no evidence that replacement of plant-available N from CAN by LCM increases short-term leaching risk, but there is some evidence pointing to the contrary, similar to the mechanisms suggested above for grassland. The N flush after grassland destruction, and the related increased leaching risk, can be avoided when grass and silage maize are not grown in rotation but each crop continuously on their own respective fields. Continuous maize cropping could however be undesirable due to negative effects on soil and crop health in the longer term.

It can be concluded that short-term nitrate leaching from LCM is in general not higher, but rather lower, than from CAN, in particular for cut grassland. Increased mineralization of accumulating organic N from LCM can potentially increase nitrate leaching in the long term. This risk can be mitigated (maize) or eliminated (grassland) when the level of supplementary CAN application is properly adjusted. When manure is not produced as LCM, but excreted in urine and dung patches during grazing, nitrate leaching is higher than from LCM or CAN, at the same level of N uptake. A reduction of the manure application limit on grassland from 250 to 230 kg N ha<sup>-1</sup>, and replacement of the difference by CAN on a NFRV-basis, will reduce nitrate leaching on drought-sensitive (sandy) soils only when this results in a decrease in manure produced during grazing. When manure is applied as LCM, replacement of the difference by CAN will rather increase nitrate leaching. A general reduction of the manure application limit on grassland from 250 to 170 kg N ha<sup>-1</sup>, and replacement of the difference by CAN on a NFRV-basis, will increase rather than decrease nitrate leaching from Dutch dairy farming, in particular for cut grassland on drought-sensitive soils

Changes in the manure application rate on grassland and silage maize can result in positive and negative trade-offs at several levels (field, farm, national, global). Potential positive trade-offs from e.g. increased manure application are an increased level of soil fertility and carbon sequestration; potential negative trade-offs are increased N losses by other pathways during the (manure) production cycle or increased P-leaching due to P-accumulation in soil. These trade-offs are outside the scope of this study, but should be further explored to fully understand life cycle effects of changes.

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# 1 Introduction

Liquid dairy cattle manure (LCM), a mixture of cow urine and faeces, currently has the reputation of being a relatively environmentally unfriendly nitrogen (N) fertilizer source if not used in a manner to manage N losses. The production and use of relatively large amounts of LCM can contribute to pollution of the atmosphere and N sensitive natural ecosystems reserves, as a result of ammonia volatilization (and subsequent N deposition) and of nitrate leaching to ground- and surface water.

In Europe, the application of N from animal manure to agricultural land is generally restricted to 170 kg total N ha<sup>-1</sup> year<sup>-1</sup>. As a derogation, this limit is increased to 250 kg total N ha<sup>-1</sup> year<sup>-1</sup>, if certain requirements are met. In addition to the restriction of animal manures (based on total N in manure), the Dutch legislation uses a separate set of restrictions: the N- and P 'application standards'. These restrictions define the allowable N and P rates from both animal manures and synthetic fertilizers. In these application standards, N in synthetic fertilizers is accounted for at 100%, whereas N in animal manures is only accounted for a synthetic fertiliser equivalent value; i.e. the N fertilizer replacement value (NFRV). For instance, if the annual apparent N recovery (ANR) of synthetic fertilizer is 0.8 and the ANR of LCM is 0.48, the NFRV value of LCM is  $(0.48 / 0.80) = 0.6$ . The N application standards vary by crop and soil type.

The difference between the application limit for total N permitted and the N supplied by manure is supplemented with synthetic fertilizer. In the case of the Netherlands, the synthetic fertilizer used is predominantly in the form of calcium ammonium nitrate (CAN). In CAN, half of the N is present as ammonium (NH<sub>4</sub><sup>+</sup>) and the other half as nitrate (NO<sub>3</sub><sup>-</sup>). In contrast to LCM, CAN is reputed to be highly efficient, with a high N use efficiency of 80-100% ([www.rvo.nl](http://www.rvo.nl)). However, there is evidence to suggest that this N use efficiency can be considerably lower on sandy soils, due to relatively high N losses after application (De Boer et al. 2016). More specifically, the nitrate in CAN appears rather sensitive to be leached to ground- and surface water shortly after application (Barraclough et al. 1983; De Boer et al. 2016) and is also susceptible to increased loss by denitrification, compared to other N sources (Harty et al. 2016). In the Dutch dairy sector, the reputed high efficiency of CAN relative to LCM is questioned, and it has been suggested that, all aspects of the life cycles of both fertilizers considered, LCM might be a more environmentally friendly fertilizer than CAN. In contrast, in a recent evaluation of the effects of manure legislation, it is suggested that the manure N application limit should be reduced and manure should be replaced by CAN on a NFRV-basis, as a strategy to reduce nitrate leaching and achieve the EU nitrate concentration limits in ground- and surface water (Van Grinsven and Bleeker 2017). As a reduction in the manure application level would have a significant impact on the Dutch dairy sector, it is necessary to assess the effectiveness of such a replacement.

Stichting Mesdag ZuivelFonds (Leeuwarden, The Netherlands), a trust financed by Dutch dairy farmers and aiming to improve the sector's performance through innovation and research, commissioned this study to assess differences in environmental performance between LCM and CAN, focussing on nitrate leaching as a first step. The objective of this study is to analyse differences in the risk and level of nitrate leaching from LCM and CAN when applied to grassland and silage maize, the main crops in Dutch dairy farming. Three questions were asked to be answered:

1. Is nitrate leaching from (shallowly-injected) LCM in general higher than from (surface-spread) CAN, when compared at the same level of N uptake?
2. Will the recent reduction in the manure N derogation limit from 250 to 230 kg total N ha<sup>-1</sup> on leaching-sensitive sandy soils in the provinces of Overijssel, Gelderland, Utrecht, Noord-Brabant and Limburg, and replacement of the difference with CAN on NFRV-basis, result in a lower level of nitrate leaching?
3. Would a general reduction in the manure N derogation limit from 250 to 170 kg total N ha<sup>-1</sup>, and replacement of the difference with CAN on NFRV-basis, result in lower nitrate leaching from Dutch dairy farms?

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## 2 Methods and scope

To answer the questions, a literature study was done to analyse the relevant mechanisms contributing to nitrate leaching from LCM and CAN and to evaluate the results from experimental studies. We focused on nitrate leaching after application of either CAN or LCM to grassland dominated by *Lolium perenne* L., either cut or grazed, and either cultivated permanently or grown in rotation with silage maize (*Zea mays* L.), the dominant arable crop on dairy farms in the Netherlands. Both crops and grassland use systems are discussed in separate chapters.

There are many factors that influence the level of nitrate leaching from agricultural soils. Most of these factors have been extensively described and reviewed, most recently by Cameron et al. (2013). The present study does not focus on the general process of nitrate leaching and analysis of the factors and their interactions involved, but mainly on the differences between LCM and CAN in nitrate leaching potential on grassland and maize, with special attention to agronomic aspects.

Factors that affect N losses, other than by nitrate leaching, can have a large effect on nitrate leaching potential from CAN or LCM. The most important factor to consider is the level of ammonia volatilization after LCM application. In the Netherlands, nearly all LCM is applied by shallow injection and CAN is surface-spread in granular form. In general, surface-spread LCM has a higher level of ammonia volatilization than injected LCM (Huijsmans et al. 2016), which can reduce the level of plant-available N, the potential inorganic N surplus and thus nitrate leaching potential. A reduction in nitrate leaching due to higher ammonia volatilization is however to be regarded as a negative trade-off. Huijsmans et al. (2016) reports an average volatilization loss of 16% of NH<sub>4</sub>-N for injected LCM versus 74% for surface-spread LCM, but it should be noted that there is ongoing debate on the reliability of ammonia measurements and reported volatilization levels (Hanekamp et al. 2017). Because injection of LCM is under most circumstances mandatory in the Netherlands, this study focusses on the comparison between shallowly injected LCM and (surface-spread) CAN.

The focus of this study is to compare nitrate leaching between LCM and CAN per unit of crop N uptake. This is considered by the author to be the most accurate basis for comparison. A comparison based on applied total N rate would not take into account differences in N availability between the two fertilizer types. A comparison based on N fertilizer replacement value (NFRV) (i.e. the part of N in LCM that works equivalent to N in CAN) could mask differences in leaching potential, because synthetic fertilizer is used as the reference in NFRV calculation.

The nitrate leaching potential of LCM could also be compared with synthetic fertilizers other than CAN, such as 100% ammonium or urea fertilizers. These comparisons could potentially lead to different results. Historically, and largely because of a higher risk of N losses by ammonia volatilization and a higher potential for soil acidification, these fertilizer types are scarcely used in the Netherlands and therefore left outside the scope of this study.

Changes in the manure application rate on grassland and silage maize can result in positive and negative trade-offs at several levels (field, farm, national, global). Potential positive trade-offs from increased manure application are an increased level of soil fertility and carbon sequestration; potential negative trade-offs are increased N losses by other pathways during the (manure) production cycle or increased P-leaching due to P-accumulation in soil. These trade-offs are outside the scope of this study, but should be further explored to fully understand life cycle effects of changes.

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## 3 Results & discussion

### 3.1 Process and mechanisms

#### 3.1.1 Nitrate leaching processes

Nitrate can be leached from a soil when it is present in the soil solution during downward water movement, or drainage. A period of prolonged drainage usually starts after the end of the growing season, in the Netherlands at the end of October, when the soil profile becomes saturated with water as precipitation starts to exceed evapotranspiration. The nitrate then present in the soil is at risk of being leached to ground- and surface water, if not taken up by a crop. Leaching to surface water can occur by subsurface lateral flow, which is stimulated when an artificial drainage system is installed, and by surface run-off (from sloping sites) during times when precipitation exceeds infiltration (Sherwood and Fanning 1981; Jarvis et al. 1987). In the absence of preferential flow pathways, nitrate leaching can be substantially higher from freely drained compared to poorly drained or undrained fields. Poor drainage usually results in a larger part of the nitrate being lost by the process of denitrification (Garwood and Ryden 1986). Drainage can also occur during the growing season, during periods of heavy or prolonged rainfall. Within a short period, rainfall water with dissolved nitrate can then rapidly drain through soil macro pores, such as soil cracks, root channels and earthworm burrows, a process referred to as preferential flow (Dekker and Bouma 1984; Kramers et al. 2012) but sometimes also as bypass flow (Scholefield et al. 1993). Nitrate that is leached below the rooting zone during the growing season not necessarily leaches further down to the groundwater, as it may also be denitrified and lost in gaseous form before it reaches the groundwater. On soils with sufficient capillary rise, part of the initially leached nitrate can be transported back in the rooting zone and taken up by the crop later. There are a number of factors influencing the amount of nitrate present in the soil at a given moment in time, and thus nitrate leaching risk. The form in which N is present in fertilizers is a decisive factor, both in the short- as well as the longer term.

#### 3.1.2 Nitrogen form and direct leaching risk

In CAN, half of the N is present as ammonium and the other half as nitrate. In LCM, as it is produced in the Netherlands, also half of the N is present in the form of ammonium but the other half as organic N (Anonymous 2017). There is a distinct difference between ammonium and nitrate in their behaviour in the soil solution, due to a difference in electrical charge. Ammonium is a cation ( $\text{NH}_4^+$ ) and nitrate an anion ( $\text{NO}_3^-$ ). In soil, cations are adsorbed to the negatively charged soil cation exchange complex (CEC) and thus largely protected from leaching (Cameron et al. 2013). In contrast, anions are not adsorbed and therefore easily leached if not taken up by the crop, immobilized in the soil or lost in gaseous form (Cameron et al. 2013). Organic N is only for a small part dissolved in the soil solution and that part can potentially be leached directly after application. The leaching risk of the three N forms is discussed in more detail below.

##### *Ammonium*

Ammonium due to its positive charge can be adsorbed onto the CEC. As a result, the amounts of leached ammonium are usually very small to negligible. Mancino and Troll (1990) concluded that ammonium losses were always negligible after application of ammonium nitrate followed by irrigation in a greenhouse study with pots. Di et al. (1998) measured less than  $1 \text{ kg ha}^{-1} \text{ year}^{-1}$  leaching of ammonium-N after application of  $2 \times 200 \text{ kg N ha}^{-1} \text{ year}^{-1}$  as ammonium chloride in a two-year field experiment on pasture. From the results of a 30-year arable crop rotation experiment, Adomaitis et al. (2008) concluded that the effect of synthetic fertilizers on ammonium concentration in lysimeter water was insignificant. Occasionally, larger amounts of ammonium leaching are reported. In an area with high rainfall, up to 14% of annual leaching and surface-runoff of inorganic N from a 40 ha catchment was in the form of ammonium; the average contribution during 8 years was 11% (Horne 1980).

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Kurz et al. (2005) reported considerable ammonium leaching during a high water flow event, two days after the application of urea fertilizer. Regardless of the behaviour of ammonium-N in view of leaching, it can be argued that CAN and LCM will not differ much in this respect if both contain about 50% of N in ammonium form.

#### *Nitrate*

Nitrate, an anion, is not adsorbed onto the CEC and therefore easily leached if not taken up by the crop, immobilized in the soil or lost in gaseous form (Cameron et al. 2013). In LCM, as it is produced in the Netherlands, half of the N is present in the form of ammonium and the other half in the form of organic N (Anonymous 2017). Ammonium and organic N are precursors of nitrate and have to be converted into nitrate for a nitrate leaching risk to occur. In CAN, half of the N is present as ammonium and the other half as nitrate. Therefore, 50% of N applied by CAN is at immediate, increased risk (relative to ammonium N) of leaching by preferential flow. There is increasing evidence that this direct nitrate leaching can seriously contribute to the annual nitrate leaching potential of nitrate-based fertilizers. Under field conditions, Barraclough et al. (1983) reported the incidence of direct nitrate leaching due to heavy rainfall (26.5 mm) on the third day after fertilizer application in April. At annual N application rates of 250 and 500 kg N ha<sup>-1</sup> as ammonium nitrate, 58 and 22% of the annual amount of nitrate leaching occurred in one week after the application of 62.5 and 125 kg N ha<sup>-1</sup>, respectively (Barraclough et al. 1983). Dekker and Bouma (1984) reported that on average 30% of fertilizer N had leached from cracked clay soil cores, when irrigated with on average 18 mm of water immediately after the application of 80 kg N ha<sup>-1</sup> as ammonium nitrate. Esala and Leppänen (1998) simulated heavy rainfall (70 mm) one day after nitrate fertilizer application at 120 kg N ha<sup>-1</sup> and reported a nitrate loss of 27% on columns of sandy soil and 23% on columns of clay soil containing earthworm burrows. Under field conditions, De Boer et al. (2016) found that a delay of CAN application on permanent grassland by 3 days or more, instead of application directly after harvest, resulted in a significant increase in N uptake and yield of the fifth growth period. This increase was attributed to heavy rainfall (29 mm) on the first day of that growth period. The difference in N uptake between the delay treatments suggested that at least 25% of applied fertilizer N was lost by leaching below the rooting zone. The rainfall amounts likely also influenced nitrate leaching and N uptake during the fourth growth period of the experiment by De Boer et al. (2016), although effects were less pronounced compared to the fifth growth period.

In many experimental studies, the actual level of nitrate leaching during the growing season is not measured. The total annual nitrate leaching (potential) is usually evaluated based on the inorganic N surplus in soil at the end of the growing season, or on nitrate concentrations in the upper groundwater in the following spring. As the amount of nitrate leached during the growing season cannot be derived from the inorganic N surplus in autumn, and its effect on nitrate concentrations in groundwater may largely have disappeared by spring, it appears that nitrate leaching risk from CAN currently is underestimated relative to LCM.

#### *Organic N*

Organic N is largely protected from leaching, because most of it does not dissolve into water. Of the organic N, only dissolved organic N (DON) can readily leach down the soil profile (Carey et al. 1997; Van Kessel et al. 2009) and possibly below the rooting zone. After leaching, conversion of DON into ammonium and then into nitrate could contribute to nitrate leaching. DON-leaching losses from grassland appear to be small (3 to 4 kg N ha<sup>-1</sup> year<sup>-1</sup>), although considerable amounts can be leached from under urine and dung patches that are deposited during grazing (Van Kessel et al. 2009).

### 3.1.3 Nitrogen form and longer-term leaching risk

Nitrogen that is present in the form of ammonium or organic N represents mainly a longer-term leaching risk due to the potential conversion into nitrate. The overall N conversion processes are described in detail by e.g. Cameron et al. (2013). In general, organic N is first converted into urea (mineralization), from urea into ammonium (ammonification) and from ammonium into nitrate (nitrification). There are some exceptions, as organic N can also be directly converted into nitrate (heterotrophic nitrification) (Zhang et al. 2015). The time it takes for different precursors to be converted into nitrate introduces a delay.

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This delay is important, because a growing crop such as ryegrass continuously takes up N as ammonium and/or nitrate during the growing season (Bailey 1998), thereby reducing the concentrations in soil. Thus, although organic N and ammonium N are eventually converted into nitrate, this delay, combined with ongoing plant uptake, reduces the leaching risk of N present in this form. The delay factor differs considerably between organic N and ammonium.

The conversion of organic N into urea and ammonium can take a considerable amount of time, depending on the complexity of the organic compounds, temperature, soil moisture, etc. For LCM, it can take many years before all organic N is mineralized. In a 4-year field experiment with shallow injection of LCM into grassland, about 35% of applied total N became available in the first year, 5% in the second, 2-3% in the third and 2-3% in the fourth (Schröder et al. 2007). As about 8% of the applied N (16% of applied ammonium-N) may have been lost by ammonia volatilization (Huijsmans et al. 2016), even after the four years of measurement up to 46% of the applied N could still have been present in the soil to be mineralized in later years, at a rate of 2-3% per year or less. Müller et al. (2011b) showed that over a 38-year period, the repeated application of LCM on grassland at a medium or high level resulted in a positive trend in grass N uptake and yield, which likely reflects the slow mineralization rate of organic N.

The slow, ongoing mineralization of organic N not only presents a short-term potential advantage, but also a longer-term potential risk. During autumn and winter, there is little or no N demand by the crop. If mineralization continues longer and/or at a larger rate than crop N uptake, mineralization of organic N during autumn and winter could increase nitrate leaching. Because organic N mineralization rate and crop N uptake rate are both controlled by temperature, and a lower temperature will reduce the rate of both processes, this risk may be small or absent in the presence of a perennial crop (such as perennial ryegrass) or when a N catch crop is grown after an annual crop (such as silage maize) (see below). A general problem with LCM is, however, that the time of release of the remaining organic N can not easily be predicted, which can result in increased leaching risk depending on crop growth and N uptake characteristics throughout the growing season.

The conversion of urea into ammonium is usually complete within 24 hours (Ball and Ryden 1984). The conversion rate of ammonium into nitrate depends on soil conditions such as temperature, soil moisture content and pH (Cameron et al. 2013). The time to completion can be as short as two weeks at high soil temperature (24°C), to longer than 12 weeks at low temperature (< 10°C) (WFH 2002), and likely takes three to six weeks during the growing season (Ball and Ryden 1984). Ryegrass appears to take up both nitrate and ammonium at identical rates and there is no clear evidence pointing to a general preference for either form (Bailey 1998). In grassland, most of the nitrate produced from ammonium during two to three weeks can be taken up by the growing crop, resulting in a reduced nitrate leaching risk from applied ammonium and organic N compared to nitrate. As LCM does not contain nitrate, but only the nitrate precursors ammonium and organic N, it becomes clear that, at the same level of N uptake, the short-term nitrate leaching risk from LCM should be smaller than from CAN. Longer term, however, this potential advantage is only realized when the mineralization rate of remaining organic N from LCM in soil is in sync with the crop N uptake rate throughout the growing season.

#### 3.1.4 Nitrate removal from the soil solution

A continuous uptake of nitrate and its precursor ammonium by a growing crop from the soil solution counters the accumulation of nitrate applied by CAN or produced through nitrification. The more vigorous crop growth, the more N and nitrate will be taken up. As long as N supply by fertilization and organic N mineralization is in sync with grass N demand, nitrate leaching risk will be low.

Apart from N removal by crop uptake, nitrate or ammonium can temporarily be removed from the soil solution by immobilization and is thus protected from leaching (Whitehead 1986; Christie and Wasson 2001; Stockdale et al. 2002). For example, Van den Heuvel et al. (1991) found that 7-17% of applied nitrate remaining in the topsoil (0 - 20 cm) was immobilized as organic N. Immobilized N can later be mineralized again and contribute to N accumulation in the soil profile (Ball and Ryden 1984). Nevertheless, Stockdale et al. (2002) showed that higher immobilization relative to nitrification reduced nitrate leaching from grassland soils. Nitrate is also removed from the soil solution by the

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microbially mediated process of denitrification (Cameron et al. 2013). In this process, nitrate is stepwise reduced to dinitrogen (N<sub>2</sub>) gas. There is an (obvious) interdependency between denitrification losses and nitrate leaching, as denitrification can result in substantial removal of nitrate from the soil profile and consequently in lower nitrate leaching. In a study by Garwood et al. (1985), freely drained soils had a higher nitrate leaching loss and lower denitrification loss compared to undrained soils. However, reduction of nitrate leaching in favour of N loss by denitrification is undesirable, as N is still lost from the agro-ecosystem and the potent greenhouse gas nitrous oxide (N<sub>2</sub>O) is formed as an intermediate in the denitrification process.

### 3.1.5 Nitrogen oversupply and leaching risk

When CAN or LCM are applied at rates above those necessary for optimum growth in the short term, the excess N is at risk of being leached as nitrate. Barraclough et al. (1983) showed under field conditions that an increase in fertilizer application rate (ammonium nitrate) on grassland from 250 to 500 and 900 kg N ha<sup>-1</sup> year<sup>-1</sup> increased nitrate leaching from 1.5 to 5.4 and 16.7% of applied N, respectively, averaged over a 3-year period. Since growth conditions largely determine the amount of grass N uptake, adverse growth conditions, such as drought, can decrease N uptake and rapidly increase nitrate leaching risk. Garwood and Tyson (1973) reported that when fertilizer N application to ryegrass, grown in lysimeters, increased from 250 to 500 kg N ha<sup>-1</sup> year<sup>-1</sup>, the leached amount of nitrate-N increased from 15 to 145 kg N ha<sup>-1</sup> year<sup>-1</sup>, averaged over a 13-year period. Peak concentrations of nitrate-N in the leachate ranged between 3-27 and 56-160 mg NO<sub>3</sub>-N L<sup>-1</sup>, respectively. The high level of N fertilization was clearly above the optimum for grass grown on this type of soil and location, particularly given the low amount of rainfall during the growing season. This resulted in nitrate accumulation in soil and consequently increased leaching risk, either during or after the growing season. In another 5-year lysimeter experiment, with different soil types, it was shown that supplementary irrigation to prevent drought stress decreased nitrate leaching loss by 26 (free-draining coarse sand) to 59% (deep loam) (Garwood and Roberts 1985). In this experiment, the annual N application rate was 420 kg N ha<sup>-1</sup> and the grass was cut nine times. In research by Webster and Dowdell (1984), simulation of dry periods during the growing season increased N leaching losses from 41 up to 104 kg N ha<sup>-1</sup> for clay loams and from 15 to 109 kg N ha<sup>-1</sup> for silt loams, respectively. In this 5-year experiment, the swards were fertilized with calcium nitrate at 400 kg N ha<sup>-1</sup> year<sup>-1</sup> and cut at intervals of six weeks during the growing season. Nitrate concentration was on average 1 mg N L<sup>-1</sup> for the unfertilized controls, increased to between 5.1 and 11.6 mg N L<sup>-1</sup> when fertilizer was applied and to 28.8 mg N L<sup>-1</sup> after a 4-week drought treatment (Webster and Dowdell 1984). It can be concluded that a relative oversupply of inorganic N, whether due to large N application rates or reduced N uptake during drought, increases nitrate leaching risk. At the end of the growing season, crop growth and therefore N uptake potential is strongly reduced. Late application of relatively large rates of CAN or LCM will therefore also result in a relative oversupply of inorganic N and should be avoided. Kolenbrander (1981) showed that nitrate leaching from synthetic fertilizer applied to grassland strongly increases when applied after July.

## 3.2 Grassland

### 3.2.1 Cut grassland

*The level of plant-available nitrogen, not the source, determines leaching risk*

Cut grassland has in general a very low nitrate leaching risk (Cameron et al. 2013), because grassland has a very large N uptake capacity compared to other crops. Under temperate climate, there is a linear relationship for *L. perenne* dominated grassland between applied fertilizer N and crop N uptake up to a rate of 450-500 kg fertilizer N ha<sup>-1</sup> year<sup>-1</sup> (Ten Berge et al. 2002; Forrestal et al. 2017). The N uptake of ryegrass also continues throughout the year, although between late autumn and early spring the N uptake capacity is relatively small (Wachendorf et al. 2006b; Malcolm et al. 2015).

For permanent grassland, it has been established that at the same NFRV, the amount of nitrate leaching is not affected by the N source, whether CAN or LCM (Ten Berge et al. 2002; Schröder et al. 2010). Therefore, Ten Berge et al. (2002) concluded that, on cut grassland, N applications as LCM up



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to 400 kg total N ha<sup>-1</sup> year<sup>-1</sup> and more have little effect on residual soil mineral N (SMN) at the end of the growing season, and therefore on the amount of nitrate leaching over winter. At this application level, every 100 kg total N applied was associated with an additional 3-4 kg autumn SMN (Ten Berge et al. 2002). However, repeated large applications of organic N will over the years result in an increase in the level of soil organic N and organic N mineralization, until a steady state is reached (Ten Berge et al. 2002; Nevens and Reheul 2005). Therefore, the level of supplementary CAN application has also to be reduced over the years, to account for this increase in plant-available N (Ten Berge et al. 2002; Schröder et al. 2010). If the level of supplementary N from CAN is not adjusted, the level of available N will start to exceed plant N uptake over the years, resulting in higher N surpluses at the end of the growing season and increased leaching. The conclusions by Ten Berge et al. (2002) were based on meta-analysis of a broad dataset, containing data from different experiments, growing seasons and locations.

The conclusions by Ten Berge et al. (2002) were based on the level of autumn SMN, and for a limited subset it was concluded that autumn SMN correlated well with measured nitrate leaching. However, in other studies this correlation was poor. For silage maize, Wachendorf et al. (2006a) reported that less than 45% of autumn SMN was leached as nitrate, whereas Müller et al. (2011a) reported that autumn SMN only accounted for 27% of the variation in nitrate leaching losses. Related to this, Wachendorf et al. (2006a) concluded that the assumption that all autumn SMN is mobile would result in a considerable overestimation of nitrate leaching losses and Müller et al. (2011a) warned that derivations from simple N field balances can lead to misjudgements about the potential risks of nitrate leaching to groundwater. Therefore, it can be concluded that the results of studies with (repeated) measurement of actual nitrate concentrations in the upper groundwater, preferably throughout the year, seem more reliable than results from studies based on autumn SMN. Given the risk of nitrate leaching during the growing season to groundwater and through draining systems to surface water, repeated measurement of actual drainage volume and nitrate contained therein likely gives the most accurate results.

#### *Suboptimal management increases leaching*

Apart from the rather low nitrate leaching levels reported by Ten Berge et al. (2002) and Schröder et al. (2010), other studies sometimes report increased nitrate leaching after application of LCM to cut grassland. It is however necessary to evaluate the design of these experiments, as often the application time and LCM rates are poorly synchronized with the grassland N uptake capacity. In some studies, LCM, or largely similar liquid manure types, were intentionally applied at the end of the growing season, to assess the nitrate leaching risk over winter (Carey et al. 1997; Smith et al. 2002). As such, these results are not representative for nitrate leaching after LCM application at an appropriate time during the growing season. These experiments do however show that LCM application at the end of the growing season should be avoided, as N supply from LCM (directly and through mineralization) at that time will usually be higher than grassland N uptake capacity, resulting in an inorganic N surplus and increased leaching risk. The same or a greater risk would however exist if synthetic fertilizer were applied.

#### *Evidence of lower leaching from LCM relative to CAN on cut grassland*

The general conclusions by Ten Berge et al. (2002) for cut grassland were confirmed in a more recent 2-year field experiment by Schröder et al. (2010) on two sandy soils, one water-retaining and the other drought-sensitive. A detailed analysis of the results also indicates that on the drought-sensitive soil not only the NFRV but also the N source (LCM or CAN) was a determinant of nitrate leaching risk. On the drought-sensitive soil, replacement of part of 340 kg N ha<sup>-1</sup> year<sup>-1</sup> applied as CAN by LCM, based on estimated level of NFRV (60%), increased crop N uptake and yield. With maximal replacement (335 kg total N from injected LCM and 139 kg N from CAN), N uptake was in both years significantly ( $P < 0.05$ ) higher, by 11 and 25% respectively, compared to the CAN-only treatment. Yield was also significantly higher (+24%) in the dry growing season of the second year. On the water-retaining site, however, the maximal replacement of N from CAN by injected LCM, on a NFRV-basis, did not affect N uptake or yield. As reported above, drought can increase the risk of nitrate leaching from CAN compared to LCM, due to a relative oversupply, because N uptake is reduced and nitrate can accumulate more rapidly in soil when CAN is the N source used.

Given the relatively slow nitrate production from N in LCM and further reduction during drought of the conversion rate of organic N into ammonium (e.g. Xiang et al. 2008) and of ammonium into nitrate

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(Haynes 1986), the nitrate accumulation rate and average nitrate concentration in soil can be even lower for LCM compared to CAN during periods of drought.

A likely similar effect of drought on nitrate leaching was observed in earlier results reported by Jarvis et al. (1987). In a 5-year field experiment with cut grassland, total N application rate was up to 580 kg fertilizer equivalent N ha<sup>-1</sup> year<sup>-1</sup>, supplied by CAN alone or by combinations of CAN and soil-injected LDM (max. rate 380 kg total N ha<sup>-1</sup> year<sup>-1</sup>). The experiment was conducted on a loamy sand. Over the 5-year period, the average nitrate leaching during autumn and winter was lower for the combination of CAN and LCM (~8%) compared to CAN alone (~13%), at the same N application rate of 580 kg fertilizer equivalent N ha<sup>-1</sup> year<sup>-1</sup>. The difference in leaching increased with increasing rate of fertilizer equivalent N up to 580 kg N ha<sup>-1</sup> year<sup>-1</sup>. Jarvis et al. (1987) explained this difference by an increase in N loss by denitrification at the end of the growing season from the combination of LCM and CAN, relative to CAN. However, it seems unlikely that this is the sole explanation, as, especially at the lower levels of available N, most if not all N would already have been taken up by the grass at the end of the growing season. Another, more likely explanation for an increased leaching loss from CAN could be an increase in nitrate accumulation under CAN relative to CAN + LCM, because of higher N availability from CAN combined with a decreased general level of N uptake due to summer drought. It should be noted that the distribution of LCM application over the growth periods was rather unfavourable from an agronomic point of view, as all LCM was applied at once in spring, at a relatively high rate. On the other hand, CAN was split in 5 to 7 dressings over the growing season. Splitting the LCM application over the growing season would probably have increased its N use efficiency by grass and have resulted in a further reduction of relative nitrate leaching. Noteworthy, the results presented by Jarvis et al. (1987) were averages of a 5-year experimental period, which means that longer-term effects of accumulating organic N from LCM were included in the comparison. Still, leaching risk from applied LCM was lower than from CAN, at the same level of NFRV.

A direct comparison between nitrate leaching from liquid manure and synthetic fertilizer was made by O'Callaghan and Flowers (1981) in a 2-year lysimeter experiment in grassland on a loam soil. They surface-applied 400 kg N ha<sup>-1</sup> year<sup>-1</sup> as CAN or 400 kg fertilizer equivalent N ha<sup>-1</sup> year<sup>-1</sup> as liquid pig manure (LPM) on loam soil lysimeters. Annual rates were split in four applications over the growing season and nitrate leaching was measured throughout the year. In the first year, with a very dry summer, N leaching was 40% relative to grass N uptake for LPM and 47% for CAN. In the second year, N leaching was 7% relative to grass N uptake for LPM and 13% for CAN. As in this experiment a direct comparison was made between liquid animal manure and CAN, per unit of N uptake (and also at similar level of annual N uptake), these results can be considered as direct evidence of lower nitrate leaching potential of liquid animal manure relative to CAN, when applied to grassland. Liquid pig manure contains a slightly higher percentage of ammonium-N than LCM and the organic N mineralizes faster. As this results in a more rapid nitrate production from LPM relative to LCM, the difference in N leaching could have been larger when LCM instead of LPM had been applied.

The general observation from experiments with replacement of CAN by LCM or LPM on cut grassland is that short-term nitrate leaching risk from LCM relative to CAN is lower, at the same level of N uptake. The difference may increase due to drought, which occurs more frequently on drought-sensitive (sandy) soils.

*Level of background leaching is often already relatively high*

The results of Ten Berge et al. (2002) and Schröder et al. (2010) reveal a relatively high level of background nitrate leaching, as can be derived from the autumn SMN on unfertilized controls. At the location with the lowest level of SMN, SMN amounts varied already between 11 and 38 kg N ha<sup>-1</sup> year<sup>-1</sup> (Ten Berge et al. 2002). Compared to these background levels, the additional contribution from applied LCM to SMN (3-4 kg ha<sup>-1</sup> 100<sup>-1</sup> kg of total N) was low. The relatively high levels of potential background leaching are surprising, as under the N-deficient conditions on the unfertilized controls a very high N-efficiency would be expected. Part of this paradox can be explained by the inability of the crop for N uptake of mineralized soil organic N in the soil layer below the rooting zone. The soil layer between 30 and 90 cm can contain considerable amounts of organic N (Schröder et al. 2010) as a result of previous cropping and other land use history.

In relation to this, results by de Boer et al. (2012) suggest an increased risk of nitrate leaching with LCM application in the long term, even under N-deficient conditions. In a 9-year crop rotation

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experiment under organic conditions, 2 years of grass/white clover mixture were followed by 1 year of silage maize and then 1 year of triticale (x *Triticosecale*). Due to injection of 120 kg N ha<sup>-1</sup> year<sup>-1</sup> with LCM in spring (no additional fertilization), autumn SMN under grass-clover (0 to 90 cm) increased by 1 kg N ha<sup>-1</sup> year<sup>-1</sup> in the first year, but by 3 kg N ha<sup>-1</sup> year<sup>-1</sup> in the ninth year. Because the cropping of silage maize in the rotation may have contributed to this increase, these results are less representative for permanent grassland. In addition, the potential nitrate leaching risk under grass-clover in the ninth year was still very small, with only 18 kg ha<sup>-1</sup> of SMN present in soil layer 0-90 cm in autumn. Nevertheless, this potential effect of LCM application in the long term may deserve some further attention.

#### *New experiments needed to assess long-term leaching risk*

Unfortunately, experiments enabling a comparison of long-term effects of shallowly injected LCM versus CAN are scarce, apart for the results reported by Jarvis et al. (1987) as discussed above. Müller et al. (2011b) reported the results of a 38-year field experiment in Northern Ireland, where permanent grassland was either fertilized with LCM, surface-spread at 135, 270 and 540 kg of total N ha<sup>-1</sup> year<sup>-1</sup>, or synthetic fertilizer urea, applied at 200 kg N ha<sup>-1</sup> year<sup>-1</sup> (Christie 1987). In this experiment, nitrate leaching was not measured and the potential for leaching could not be derived from other measurements. The N use efficiency from LCM was low, with an average N recovery of 40, 42 and 39% for the respective increasing LCM rates and 58% for urea (Christie 1987). The surface spreading of LCM likely resulted in relatively high N loss by ammonia volatilization (Huijsmans et al. 2016) and the grass was only harvested three times annually, which could have reduced N uptake capacity. As a result, likely more N became available after fertilization than the crop needed short-term, especially at the highest LCM rate (Christie 1987; Christie and Beattie 1989). Because synthetic fertilizer urea does not contain nitrate, it is not comparable to CAN. The results of this long-term study are therefore not useful to assess potential differences in N recovery and potential nitrate leaching between CAN and injected LCM. Noteworthy, Müller et al. (2011b) observed that, after 38 years, the contribution of heterotrophic nitrification to total N mineralization greatly increased. During heterotrophic nitrification, organic N is directly oxidized by bacteria into nitrate (Zhang et al. 2015). At the highest LCM application rate, an estimated 75% of mineralized N became directly available as nitrate instead of ammonium. Because mineralization is a gradual process, largely countered by crop N uptake during the growing season, it seems unlikely that the risk of nitrate leaching would increase as a result.

In another longer-term experiment, CAN application at 180 and 360 kg N ha<sup>-1</sup> year<sup>-1</sup> was compared with surface-spread LCM at 180, 360 and 540 kg total N ha<sup>-1</sup> year<sup>-1</sup> over a 5-year period (Boon and Deventer 1977). In this experiment, nitrate leaching was also not measured and the potential for leaching could not be derived from other measurements either. The sward contained N-fixing white clover (*Trifolium repens* L.), there were differences in grazing intensity between treatments and LCM was applied at very large application rates (single application of up to 100 m<sup>3</sup> ha<sup>-1</sup>). In another 5-year study by Unwin and Smith (1983), the annual surface application of 200 kg total N ha<sup>-1</sup> with LCM (~100-120 kg fertilizer equivalent N) or 125 N ha<sup>-1</sup> as ammonium nitrate resulted in leaching of only 10 kg N ha<sup>-1</sup>. When the annual LCM application rate was increased to 800 kg N ha<sup>-1</sup> year, split in four applications during the growing season, the leaching loss increased to between 15 and 30 kg N ha<sup>-1</sup>. This was about half the loss from 500 kg N ha<sup>-1</sup> applied as ammonium nitrate, also split in four applications over the growing season. The lower loss was likely due to higher N losses by other pathways. Ryden (1986) explained the low level of nitrate leaching at the high LCM rate by a high ammonia volatilization loss following surface application, additional loss of nitrate by denitrification and a limited mineralization of organic N. Therefore, the results of this experiment are also not useful to compare longer-term effects of replacement of CAN by (injected) LCM.

The general observation is that available longer-term field experiments with separate and repeated application of LCM and CAN have too many complicating circumstances to enable an accurate comparison. The LCM is surface-applied and often under suboptimal agronomical conditions. This prevents a reliable comparison of nitrate leaching risk between CAN and LCM, used optimally, at the same level of N uptake. The only exception are the results reported by Jarvis et al. (1987), which show a lower leaching risk from applied LDM (~8%) compared to CAN (~13%), averaged over 5 years, at the same NFRV level. To make accurate comparisons, new, long-term field experiments are needed, in which N use efficiency and nitrate leaching after repeated application of only LCM, only CAN

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and combinations of LCM and CAN are compared, with both fertilizers applied under their agronomical optimal conditions. A control treatment should also be included to take background leaching into account. The results of such experiments would be useful to fine-tune management of LCM in agronomic systems in a sustainable manner over the long-term.

#### *Leaching risk after grassland renovation*

Although the level of nitrate leaching from cut grassland can be very low, the leaching risk can increase when grassland is renovated and the existing sward destroyed. Velthof et al. (2009) showed that leaching risk increases with renovation in autumn, but not in spring. Annually repeated large applications of organic N with LCM can increase the soil organic N content and thus the potential amount of N mineralization after grassland renovation. However, there is no evidence to suggest this will increase nitrate leaching risk. Renovation in spring and adjustment of the additional N fertilization will likely mitigate any risk. Additionally, no-tillage or minimum-tillage renovation could further reduce nitrate leaching risk. For other situations than reseeding, e.g. when renovation is followed by arable cropping (such as silage maize), the nitrate leaching risk could increase when higher levels of LCM are applied, although this would also largely depend on other management practices (see paragraph 3.3).

### 3.2.2 Grazed grassland

#### *Nitrate leaching risk higher with grazing compared to cutting*

On a dairy farm with cut grassland only, the urine and faeces produced by dairy cows in the barn is mixed in LCM and, after storage, evenly distributed by shallow injection over the field. As a result, nitrate leaching from LCM can be very low (Ten Berge et al. 2002), if good agronomic practices are applied. Grassland is often not only cut but also grazed. With grazing, however, cows deposit their urine and faeces separately and randomly in patches across the field during the grazing season. This uneven distribution results in a decreased N use efficiency and therefore increased nitrate leaching risk from the urine patch in particular, compared to cut grassland, at the same level of available N. Dairy cow urine patches contain between 200 and 2000 kg N ha<sup>-1</sup>, on average 613 kg N ha<sup>-1</sup> (Selbie et al. 2015) and an overlap will further increase local N concentration. Part of the deposited urinary N will volatilize as ammonia, part will be nitrified and lost by denitrification and part by nitrate leaching (Jarvis et al. 1987). Under dung patches, a considerable amount of inorganic N may also be present; Garwood and Ryden (1986) reported average nitrate and ammonium concentrations of 53.5 and 56.3 µg N g<sup>-1</sup> of soil under urine patches and 26.2 and 13.1 µg N g<sup>-1</sup> of soil under dung patches, up to a depth of 30 cm. Although the grass area influenced by a urine patch is often more than twice the area actually covered (Whitehead 1986), the grass around will have difficulty to absorb most of this N, even when a patch is deposited early in the growing season. Lantinga et al. (1987) calculated an average rate of N application to an area affected by urination of 500 kg N ha<sup>-1</sup> year<sup>-1</sup>. As the growing season advances, the remaining grass N uptake potential for newly deposited urinary N decreases and nitrate leaching risk increases. Of urine patches deposited in summer or later, only a small part of the N can be taken up, leaving a large part at risk of being lost as nitrate over the winter. Lantinga et al. (1987) noted that urinary N effects on grass growth may last for about 5 months after deposition in spring and for about 10 months after deposition in autumn. The differences in distribution of excreted N between cut and grazed grassland usually results in a large difference in the level of nitrate leaching; Kolenbrander (1981) reported that nitrate leaching losses from N deposited during grazing are 3.5 (clay soil) to 5 times (sandy soil) greater than from cut swards. Ryden (1986) showed that at the same level of CAN application (420 kg N ha<sup>-1</sup> year<sup>-1</sup>), nitrate leaching increased from 33 to 160 kg N ha<sup>-1</sup> year<sup>-1</sup> due to grazing instead of cutting. In both examples, part of the increase in nitrate leaching with grazing was due to the higher level of N input in the grazed system. Nevens and Reheul (2003) estimated, based on results of 19 studies from literature, that the EC Nitrates Directive limit of 50 mg L<sup>-1</sup> is with grazing exceeded at an inorganic N input of 150 kg ha<sup>-1</sup> year and with cutting at 450 kg inorganic N ha<sup>-1</sup> year<sup>-1</sup>.

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For an accurate comparison of differences in nitrate leaching between cut and grazed grassland, annual N input from animal manure (and applied CAN) should be similar for both systems. To our knowledge, results of experimental studies based on this principle are currently lacking. From urine and dung patches, also considerable amounts of DON can leach and potentially contribute to nitrate pollution. Van Kessel et al. (2009) give an example, where 23 (dung) to 127 (urine) kg DON ha<sup>-1</sup> year<sup>-1</sup> was leached, after local application of 1052 kg N ha<sup>-1</sup> year<sup>-1</sup> as dung and 1032 kg N ha<sup>-1</sup> year<sup>-1</sup> as urine, respectively (Wachendorf et al. 2005).

#### *Grazing management most effective to reduce leaching*

As concluded earlier in this study, a reduction in the application rate of CAN relative to LCM can be rational for cut grassland, because CAN is more sensitive to leaching. However, when manure is not applied as LCM but (partly) excreted during grazing, the nitrate leaching risk will be lower for CAN than for excreted available N (Ryden 1986), due to its more even distribution and higher N use efficiency. Therefore, a reduction in grazing intensity (and production of urine and dung patches) will be more effective to reduce nitrate leaching than a reduction in the level of available N from LCM or CAN applied, especially on drought-sensitive soils. Furthermore, a reduction in CAN application will reduce nitrate leaching more than a reduction in LCM application.

Increased nitrate leaching due to grazing can be effectively reduced by putting an earlier end to the grazing season. Ketelsen et al. (1999) suggested that nitrate concentrations in drainage water could be reduced by 40% by limiting the daily grazing time to 9 hours and ending the grazing season in mid-September in Germany, where weather conditions are largely similar to the Netherlands. De Boer (2005) showed for a drought-sensitive sandy soil in the Netherlands that ending the grazing season at the end of June instead of mid-October reduced nitrate concentration in the upper groundwater from 48 to 32 mg NO<sub>3</sub> L<sup>-1</sup> the following spring. Other practices to reduce nitrate leaching due to grazing could be the use of tactical fertilization strategies (Hack-Ten Broeke et al. 1997; Cuttle et al. 2001), reduction of the dietary nitrogen content (Van Vuuren and Meijs 1987), reduction of the grazing intensity (De Klein 2001; Anger et al. 2002) or restricted grazing (Christensen et al. 2012) while achieving a similar level of grass uptake in a shorter grazing time (Kennedy et al. 2011).

### 3.3 Silage maize

#### *Silage maize uses mineralized organic nitrogen inefficiently*

Silage maize (*Zea mays* L.) is the second most important crop grown on Dutch dairy farms after grassland. It is grown in rotation with grassland or continuously. When grown in rotation, the grassland is usually destroyed by ploughing in spring, followed by maize sowing. The organic N mineralization flush due to grassland destruction can produce more N (over 200 kg ha<sup>-1</sup>) (Velthof et al. 2009) than the maize crop needs or is able to absorb (~150 - 200 kg N ha<sup>-1</sup> year<sup>-1</sup>) (Pollmer et al. 1979; Wachendorf et al. 2006b).

A remarkable characteristic of maize is that its N uptake period is rather short. In the Netherlands, maize is sown between late April and early May. It takes about 6 weeks after sowing before plants reach the 6-8 leaf stage and N demand starts to increase to a significant level (Sticksel et al. 1994). Nitrogen uptake, however, declines again at the tasseling/silking stage (Pollmer et al. 1979; Plénet and Lemaire 2000) and ceases either around tasseling (Pollmer et al. 1979) or about a month later (Plénet and Lemaire 2000). Tasseling occurs in the Netherlands in mid-July, 2-3 months before harvest (Ten Berge et al. 2007). As a result, the period with increased N uptake only lasts an estimated 4 to 6 weeks during the growing season.

A large part of the inorganic N that is present in the soil around mid-July, and of the organic N that mineralizes afterwards, can be converted into nitrate and leached, due to the declining N uptake rate of maize during reproductive growth. These N uptake characteristics of maize would suggest that LCM is an unsuitable fertilizer for maize, unless additional measures are taken to offset the rather inefficient use of (mineralized) N. Because of the low N use efficiency of maize compared to permanent (cut) grassland, maize can disproportionately contribute to nitrate leaching of a grass-maize rotation. For example, in a 9-year field experiment with rotation of grass-clover and maize, autumn SMN (0 - 90 cm) was up to 30 kg ha<sup>-1</sup> after grass-clover but 40 - 60 kg N ha<sup>-1</sup> after silage maize (De Boer et al. 2012). The low N use efficiency of maize is also demonstrated by results of a field experiment with continuous cropping of silage maize (2003 - 2008), either unfertilized or fertilized

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with farmyard manure or LCM (De Boer, unpublished). Despite an obvious N shortage during the growing season, autumn SMN (0 - 90 cm) was rather higher than lower for the unfertilized control (70 kg N ha<sup>-1</sup>) compared to the fertilized treatments (56 kg N ha<sup>-1</sup>). The N shortage was reflected in the yield of the unfertilized control treatment, which decreased from 15.8 to 2.8 Mg DM ha<sup>-1</sup> year<sup>-1</sup> over 6 years. In addition to nitrate leaching, DON-leaching can also be higher from grass/maize rotations when compared to permanent grassland. Siemens et al. (2002, 2003) reported losses of about 9 kg DON ha<sup>-1</sup> year<sup>-1</sup> for grass-maize rotations, which compare to 3-4 kg DON ha<sup>-1</sup> year<sup>-1</sup> found for permanent grassland (Van Kessel et al. 2009).

The N mineralization flush after grassland destruction can be avoided when grass and silage maize are not grown in rotation, but each crop continuously on their own respective fields. High rates of LCM application on the grassland fields then will not potentially contribute to increased nitrate leaching potential at farm level (i.e. the sum of two separate crops), provided that the level of additional N fertilization on grasslands is adjusted to account for increased mineralization of organic N over the years. However, continuous maize cropping may negatively affect soil and crop health in the longer term and can therefore be undesirable from that perspective (Van Eekeren et al. 2008).

#### *Manure application does not increase nitrate leaching from maize in the short term*

No results were found to indicate that, in the short-term, nitrate leaching potential after maize is higher when LCM is applied instead of CAN. In their 4-year field experiment, Wachendorf et al. (2006ab) reported no clear differences in nitrate leaching between LCM and CAN, although it should be noted that leachate nitrate concentration was relatively low after only CAN application up to a level of 150 kg N ha<sup>-1</sup> (40 mg NO<sub>3</sub> L<sup>-1</sup>). Although nitrate concentration after only LCM application was lower (~25 mg L<sup>-1</sup>) up to 40 Mg of LCM ha<sup>-1</sup>, yield level was also lower. The results by Wachendorf et al. (2006ab) do not enable to make a clear comparison of the level of nitrate leaching between CAN and LCM, at the same level of N uptake. In a 2-year field experiment by Schröder et al. (2013), the N yield of the first growing season was comparable for LCM and CAN (~180 kg N ha<sup>-1</sup>), but groundwater nitrate concentration in the following spring (without growing a catch crop) was lower for LCM (119 mg NO<sub>3</sub> L<sup>-1</sup>) compared to CAN (156 mg NO<sub>3</sub> L<sup>-1</sup>). After the second growing season, nitrate concentration in spring was higher for LCM (101 mg L<sup>-1</sup>) compared to CAN (73 mg L<sup>-1</sup>), but N yield was also much higher for LCM (175 kg N ha<sup>-1</sup>) compared to CAN (133 kg N ha<sup>-1</sup>). It is unclear why the average NFRV of LCM (79%) was higher than usual (60%) (Schröder et al. 2013), but a higher nitrate leaching loss from CAN due to drought on this sandy soil could have been the cause, similar to the mechanism suggested for grassland. High rainfall directly after CAN application could also have contributed to the difference in leaching between CAN and LCM.

The general observation from experiments with application of CAN or LCM to silage maize suggests that replacement of CAN by LCM does not increase leaching risk in the short term and may have potential to reduce this risk, at the same level of plant N uptake, similar to the mechanism suggested for grassland.

#### *Manure application can increase leaching risk from maize in the longer term*

Over the years, relatively high repeated LCM applications can increase soil organic N level. Increased mineralization of this accumulated organic N could increase nitrate leaching potential from maize crops, if supplementary CAN fertilization is not adapted. Results from a longer-term experiment with continuous maize cultivation showed that nitrate accumulation in autumn, in the sixth year of the experiment, was greater in a manured system (135 kg N ha<sup>-1</sup> year<sup>-1</sup>) than in a non-manured system (115 kg N ha<sup>-1</sup> year<sup>-1</sup>) at the economic N application rate for synthetic fertilizer (Roth and Fox 1990). In this experiment, LCM had been applied for 6 years at an average rate of 172 kg total N ha<sup>-1</sup> year<sup>-1</sup>. Other sites with a history of manure application also had on average higher nitrate accumulation (94 kg N ha<sup>-1</sup>) than previously unmanured sites (74 kg N ha<sup>-1</sup>) (Roth and Fox 1990). These results indicate that potential nitrate leaching can be higher after repeated LCM application. However, it should be noted that the economic N application rate is usually relatively high (as the price of fertilizer N is relatively low) and higher than the environmentally optimal application rate. A lower N fertilization level would have resulted in a reduction of supplementary CAN fertilization and thus in leaching risk.

In contrast to the results by Roth and Fox (1990), Nevens and Reheul (2005) did not find a difference in SMN between treatments with and without LCM application, at supplementary CAN application levels in the range of 50 kg N ha<sup>-1</sup> of the economical optimal rate. Based on their 19-year

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experiment with continuous maize cropping, they concluded that LCM application of 180 kg total N ha<sup>-1</sup> year<sup>-1</sup> and supplementary CAN application of 90 kg N ha<sup>-1</sup> year<sup>-1</sup> resulted in an economical optimal N fertilization on this sandy soil. When the supplementary CAN application was reduced by 50 kg N ha<sup>-1</sup> year<sup>-1</sup>, autumn SMN could be reduced below 60 kg N ha<sup>-1</sup>, with a yield loss of maximal 5%. The results of Nevens and Reheul (2005) show that adjustment of supplementary CAN fertilization to the level of organic N mineralization (a strategy applied in the Netherlands) can mitigate the risk of increased leaching due to accumulation of organic N.

An interesting discussion point is whether increased leaching risk due to accumulation of organic N should be assigned to an application of 'too much' LCM, or rather to the seasonal N uptake profile characteristics of the maize crop. Other fodder crops have a much longer N uptake period over the growing season; for instance fodder beet (*Beta vulgaris* L.) absorbs N into late autumn and the level of annual N uptake can approach 500 kg N ha<sup>-1</sup>-year<sup>-1</sup> (Nevens and Reheul 2005), close to N uptake capacity of permanent grassland (Ten Berge et al. 2002).

#### *Management affects leaching more than site conditions and fertilization history*

Kayser (2008) stated that, although nitrate leaching after grassland destruction and crop sowing is influenced by site conditions and grassland management prior to destruction, the management afterwards is more decisive. In the Netherlands, it is still common practice to fertilize maize grown after grassland destruction with LCM and/or CAN. As the maize crop usually does not need this additional N to achieve a sufficient yield level (Ten Berge et al. 2007; Van Schooten et al. 2016), additional fertilization should be minimized or avoided, as it further and unnecessarily increases nitrate leaching risk.

The application of LCM or CAN before sowing also increases (direct) nitrate leaching risk, as it takes about 6 weeks before plant N demand starts to increase to a significant level (Sticksel et al. 1994). Postponement of the first N fertilization from around sowing to the 6-8 leaf stage therefore has potential to reduce direct nitrate leaching risk without yield loss (Sticksel et al. 1994). If LCM or CAN is applied before sowing, it should rather be banded in the plant row than evenly applied over the field, to increase local N availability and uptake efficiency and reduce potential nitrate leaching (Schröder et al. 2015). Doing a pre-sidedress soil nitrate test when the plants are 15 to 30 cm high, to determine the supplementary synthetic N requirement (Meisinger et al. 1992), could further increase N use efficiency and decrease leaching risk. An additional contribution could be realized by the choice of specific maize varieties or by harvesting earlier (Müller et al. 2011a).

An increased uptake of mineralized organic N after tasseling, a period when the N uptake of maize is declining, can be realized by undersowing or after sowing of a N catch crop, such as ryegrass or a winter cereal crop, without starter N. Undersowing at the V3 to V4 maize leaf stage (30 - 50 cm height) results in an established grass crop directly after harvest with a relatively large N uptake potential. Wachendorf et al. (2006b) reported a N uptake of undersown perennial ryegrass of 50-68 N ha<sup>-1</sup> year<sup>-1</sup>, of which only 10% potentially also could have been used by the maize crop. Undersowing can reduce nitrate leaching by on average 50% (Wachendorf et al. 2006a), provided the catch crop is established properly (Hansen and Eriksen 2016). A catch crop sown after harvest (end of September) has limited time to develop before the onset of winter and therefore has a smaller N uptake potential. Still, an amount of 25 kg N ha<sup>-1</sup> year<sup>-1</sup> can be taken up and transferred to the next growing season, if the crop is destroyed in March of the next year (Van Schooten et al. 2016). Results by Schröder et al. (2013) show that the aftersowing of rye (*Secale cereale* L.) reduced nitrate concentration in the upper groundwater in spring from on average 90 mg NO<sub>3</sub> L<sup>-1</sup> to 47 mg NO<sub>3</sub> L<sup>-1</sup>, at a N fertilization level of 150 kg plant-available N ha<sup>-1</sup> year<sup>-1</sup>. Given the increased risk of nitrate leaching with maize cultivation, and the potential of catch crops to reduce leaching, growing a catch crop after maize is now compulsory in the Netherlands.

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# 4 Conclusions

## Leaching process and mechanisms

- There are some fundamental differences in short- and longer term nitrate leaching risk between LCM and CAN due to a difference in N formulation. In CAN, half of the N is present as ammonium and the other half as nitrate. In LCM, half of the N is also present as ammonium but the other half as organic N
- During the growing season, nitrate is at increased risk of direct leaching by preferential flow through soil macro pores, following a period of prolonged or heavy rainfall. As half of the N in CAN is already present as nitrate, this nitrate is at immediate risk of being leached
- With LCM, however, organic N has to be converted to ammonium, and from ammonium into nitrate, before leaching as nitrate can occur. Both conversions can take considerable time, during which nitrate accumulation is countered by plant N uptake. As plant uptake reduces the average nitrate concentration in soil, the nitrate leaching risk during the growing season can be smaller for LCM than CAN when applied to crops, such as grass, with ongoing N uptake during the growing season.
- It is unclear from current evidence whether the potential in-season advantage of LCM is offset by the increased (post-season) leaching risk arising from mineralisation of the organic N pool, a pool that increases over the years under repeated LCM application. Such offset is likely to occur under maize (as maize N uptake has declined or ceased during mid-summer, when soil N mineralization is active) and less likely under grassland (with its prolonged N uptake throughout the growing season, during the period with most active N mineralization)
- In experimental studies and their interpretation, the contribution of nitrate leaching during the growing season is rarely considered. Consequently, (direct) nitrate leaching risk from CAN appears underestimated relative to LCM
- Nitrate leaching risk increases when inorganic N is applied or becomes available at rates higher than necessary for optimum growth. As drought reduces plant N uptake, this can also result in a relative oversupply of inorganic N, accumulation of nitrate in soil and increased nitrate leaching when leaching loss pathways become active. As organic N in LCM is only slowly converted into nitrate, and the conversion rate is even more reduced during drought, the difference in leaching may increase due to drought, which occurs more frequently on drought-sensitive (sandy) soils.

## Cut grassland

- For cut grassland, the available evidence suggests that replacement of CAN by LCM decreases short-term nitrate leaching, at the same level of N uptake (O'Callaghan and Flowers 1981; Jarvis et al. 1987; Schröder et al. 2010)
- On cut grassland, the level of leaching from LCM is low and 400 kg N ha<sup>-1</sup> year<sup>-1</sup> or more can be applied without increased leaching risk in the short term, provided good agronomic practices are applied. However, an increase in the amount and mineralization of soil organic N over the years (until a steady state is reached) necessitates a reduction of the supplementary CAN application over the years, to prevent a relative oversupply of inorganic N and an increased nitrate leaching risk
- There is a lack of data from long-term grassland experiments with separate and repeated application of (injected) LCM or CAN, and combinations of both fertilizers, to be used for a full, integrated evaluation of nitrate leaching potential of these individual fertilizers in the long term



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## Grazed grassland

- Grassland grazing instead of cutting can strongly increase nitrate leaching risk, as the N in urine and faeces is not evenly spread over the field (as with LCM), but randomly deposited in patches. Especially under urine patches, the inorganic N concentration is on average higher than can be absorbed by the affected grass during the remainder of the growing season, leaving the surplus at risk of being leached
- Therefore, managing grazing intensity will be more effective to decrease nitrate leaching than a reduction in LCM or CAN application

## Silage maize

- Maize has a short period with increased N uptake during the growing season, which lasts an estimated 4 to 6 weeks. Nitrogen uptake declines afterwards and ceases mid-summer. The inorganic N present in soil and mineralizing after, during the period with declining or absent crop N uptake, is prone to leaching. As a result, maize has a low N use efficiency, especially relative to cut grassland
- When maize is grown in rotation with grassland, the low N use efficiency easily results in an oversupply of inorganic N and increased nitrate leaching from the rotation, especially in the first year, due to the mineralization flush after grassland destruction. A high level of LCM application during the grassland phase can further increase nitrate leaching risk during the arable/maize phase, as part of the applied organic N mineralizes after the cessation of maize N uptake
- A relatively high level of LCM application to maize, replacing CAN on a NFRV-basis in the first year, therefore likely increases nitrate leaching risk in the longer term, although management practices can have a larger effect on potential nitrate leaching after maize than site conditions or previous fertilization history
- There is no evidence that replacement of plant-available N from CAN by LCM increases short-term leaching risk, but there is some evidence pointing to the contrary, similar to the mechanisms suggested above for grassland
- The N flush after grassland destruction, and the related increased leaching risk, can be avoided when grass and silage maize are not grown in rotation but each crop continuously on their own respective fields. Continuous maize cropping could however be undesirable due to negative effects on soil and crop health in the longer term

## Answers to the questions

A purpose of this report was to investigate three specific questions:

1. Is nitrate leaching from LCM in general higher than from CAN, when compared at the same level of N uptake?
  2. Will the recent reduction in the manure N derogation limit from 250 to 230 kg total N ha<sup>-1</sup> on leaching-sensitive sandy soils in the provinces of Overijssel, Gelderland, Utrecht, Noord-Brabant and Limburg, and replacement of the difference by CAN on NFRV-basis, result in a lower level of nitrate leaching?
  3. Would a general reduction in the manure N derogation limit from 250 to 170 kg total N ha<sup>-1</sup>, and replacement of the difference with CAN on NFRV-basis, result in lower nitrate leaching from Dutch dairy farms?
- Answer to question 1: short-term nitrate leaching from LCM is in general not higher, but rather lower, than from CAN, in particular for cut grassland. Increased mineralization of accumulating organic N from LCM can potentially increase nitrate leaching in the long term. This risk can be mitigated (maize) or likely eliminated (grassland) when the level of supplementary CAN

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application is properly adjusted. When manure is not produced as LCM, but excreted in urine and dung patches during grazing, nitrate leaching from grassland is higher than from LCM or CAN, at the same level of N uptake.

- Answer to question 2: a reduction of the manure application limit on grassland from 250 to 230 kg N ha<sup>-1</sup>, and replacement of the difference by CAN on a NFRV-basis, will reduce nitrate leaching on drought-sensitive (sandy) soils only when this results in a decrease in manure produced during grazing. When manure is applied as LCM, replacement of the reduction by CAN will rather increase nitrate leaching
- Answer to question 3: a general reduction of the manure application limit on grassland from 250 to 170 kg N ha<sup>-1</sup>, and replacement of difference by CAN on a NFRV-basis, will increase rather than decrease nitrate leaching from Dutch dairy farming, in particular for cut grassland

### **Trade-offs**

- Changes in the manure application rate on grassland and silage maize can result in positive and negative trade-offs at several levels (field, farm, national, global). Potential positive trade-offs from e.g. increased manure application are an increased level of soil fertility and carbon sequestration; potential negative trade-offs are increased N losses by other pathways during the (manure) production cycle or increased P-leaching due to P-accumulation in soil. These trade-offs are outside the scope of this study, but should be further explored to fully understand life cycle effects of changes.

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To explore  
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