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Leached nitrate under fertilised loamy soil originates mainly from mineralisation of soil organic N

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ABSTRACT

Animal manures are suspected to be a major source of nitrate leaching due to their low nitrogen use efficiency (NUE) by crops. However, actual measurements of nitrate leaching from animal manure under field conditions are scarce. In an on-farm field trial in Switzerland over 2.5 years, we used ^{15}N labelling to trace the fate of N from cattle slurry in the soil-plant system and to test whether more nitrate was leached from slurry than from mineral fertiliser. The experiment was conducted on two neighbouring fields with loamy soil in an agricultural area of the Swiss midlands, where nitrate levels in the groundwater are persistently high. Both fields followed the same crop rotation (silage maize – winter wheat – grass-clover), but shifted by one year. We compared three fertiliser treatments: Control (Con), ^{15}N mineral fertiliser (Min), and ^{15}N cattle slurry (Slu). In order to provide a comprehensive fertiliser N balance over several years, we traced the labelled fertilisers into crop biomass, soil, and leached nitrate. In the year of application, ^{15}N recovery in crops was 45–47% for Min, but only 19–23% for Slu. Complementary to this finding, recoveries in soil were greater for Slu than for Min, despite greater NH_3 emissions from Slu. Fertiliser recovery in the succeeding crops was small ($<$ 4.6% of the originally applied fertiliser N in the first residual year and $<$ 2.4% in the second) and similar for both fertilisers. Depth translocation of fertiliser N was marginal, with the majority of ^{15}N in soil still in the top 0.3 m after 2.5 years. Along with higher recoveries in soil for Slu, we found significantly more slurry N than mineral fertiliser N lost through leaching. However, less than 5% of cumulated amounts of nitrate leaching over the three crops, which reached up to 205 kg nitrate-N ha^{-1}, originated from direct leaching of the labelled fertilisers. Our findings suggest that most nitrate leaching originated from the mineralisation of soil N.

1. Introduction

In many regions across Europe, nitrate (NO_3^-) levels in groundwater exceed quality criteria or even legal threshold values for use as drinking water (Grizzetti et al., 2011). In Switzerland, 15–20% of all groundwater measuring points and 40% of those under arable land exceed the Swiss quality criterion of 25 mg NO_3 L^{-1} (BAFU, 2019). Since nitrate is harmful to both human health (Ward et al., 2018) and natural ecosystems (Galloway et al., 2003; Erisman et al., 2013), mitigation of nitrate leaching is crucial. At the same time, nitrogen (N) is usually the limiting factor for plant growth. Thus, crop productivity depends on N input with either mineral or organic fertilisers, such as animal manure. Optimisation of N use efficiency (NUE) in agriculture, here defined as fertiliser recovery in crops, is therefore needed for agronomic as well as environmental reasons.

Animal manures are suspected to be a major source of nitrate leaching. In areas with high animal densities, there is frequently a nutrient surplus (e.g. Dalgaard et al., 2012, Oenema and Tamminga, 2005). Thereby, nitrate leaching losses often increase exponentially with N surplus (Wang et al., 2019; Zhao et al., 2016). But even when applied according to current fertilisation recommendations, animal manures have a consistently low NUE. A considerable share of N in manure is in organic form, thus, not directly available to plants, while the ammonium (NH_4^+) in the manure is prone to ammonia (NH_3) volatilisation or temporal immobilisation Thus, only about 26 ± 10% of N in animal manures are taken up by the crop in the year of application (Smith and Chalk, 2018). Organic N in manure might be mineralised at times when plants are not readily taking it up, increasing the potential for nitrate leaching

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compared to mineral fertiliser (e.g. Sørensen and Jensen, 2013, Bergström and Kirchmann, 2006, Thomsen et al., 1997). Overall, the fate of N from animal manure not taken up by crops remains poorly understood, and its contribution to nitrate loads in the groundwater is debated.

Following ^{15}N labelled fertiliser inputs throughout the soil-plant-atmosphere system over several years can enhance our understanding of N uptake and loss dynamics and pathways, helping to improve management strategies. Reviewing numerous ^{15}N labelling studies, Gardner and Drinkwater (2009) found that refined timing, splitting and placing of synthetic fertilisers can increase N uptake into crops by up to 43%, reducing the potential for nitrate leaching losses. However, they also found that despite lower N recovery of organic fertilisers, such as animal manure in crop biomass, combined recovery in crop biomass and soil was greater for organic fertilisers as compared to mineral fertiliser. Thus, recoupling carbon (C) and N in agroecosystems could contribute to reducing nitrate leaching, and therefore leaching losses might not necessarily be greater for animal manure than for mineral fertiliser, but experimental verification is missing.

So far, only a few studies have measured nitrate leaching from ^{15}N labelled animal manure, and most of these studies were conducted using lysimeters and based on pasture systems (Chalk et al., 2020). In a field experiment, Jayasundara et al. (2010) measured nitrate leaching from ^{15}N labelled swine manure under maize using suction cups. We are unaware of any study directly measuring nitrate leaching losses from ^{15}N labelled cattle slurry under field conditions during an arable crop sequence. In addition, previous field studies with ^{15}N labelled animal manure focused on either gaseous or leaching losses but did not provide a complete ^{15}N balance with all potential N uptake and loss pathways measured. ^{15}N not recovered in biomass, soil or the measured loss pathway was then assumed to have been lost via NO_3 leaching and/or as NH_3 or nitrous oxide (N_2O) gaseous emissions. However, estimates remain somewhat vague by this indirect approach. Clough et al. (1998) represent an exception, having measured fertiliser recovery in the crop, nitrate leaching, N_2O emissions, NH_3 volatilisation and soil over 406 days after application of ^{15}N labelled urine to lysimeters. Despite their efforts, the fate of 20–30% of added urine N remained unresolved, calling for further investigations.

Improved management of animal manure involves adequately considering their residual effect beyond the year of application, arising from organic N that has not yet been mineralised and from mineral N that was temporarily immobilised (Schröder et al., 2013). Recovery of different types of animal manure in subsequent crops is generally low, ranging between 3% and 6% of total applied N in the second year and between 1% and 2.5% in the third year (Webb et al., 2013). With repeated manure applications, residual manure N accumulates in the soil, increasing total N and mineral N stocks in soil and mineralisation rate (Glendining et al., 1996; Schröder et al., 2013; Schröder et al., 2005; Webb et al., 2013). If the mineralisation of accumulated N is not considered in current fertilisation, the risk for nitrate leaching increases (Edmeades, 2003). Nevertheless, mineralisable organic N in the soil cannot be readily measured and further depends, amongst others, on the nature of the manure itself, soil (texture) and climatic conditions (Schröder et al., 2013; Bhogal et al., 2016). Thus, recommendations for farmers on how to consider the residual fertiliser effect of (repeated) animal manure applications can only be based on models. Data for informing such models can be obtained by several means, with ^{15}N labelling being the least variable method (Cusick et al., 2006; Berntsen et al., 2007).

The main objectives of this study were to assess i) the NUE of animal manure and mineral fertiliser both in the year of application and during the following crops, ii) their N retention in soil as well as iii) N losses via nitrate leaching. To this end, we conducted a microplot study over three vegetation periods in which we used ^{15}N labelled mineral fertiliser (Min) and ^{15}N labelled cattle slurry (Slu). The study was located in an agricultural area of the Swiss midlands, in which groundwater nitrate levels persistently exceed the Swiss quality criterion (Gerber et al., 2018). The region is characterised by mixed crop-livestock farms with arable production and vegetable farms and has a high annual rainfall (>1000 mm $year^{-1}$), increasing the potential of nitrate leaching. Overall, we aimed to provide insights into the fate of N from cattle slurry in comparison to mineral fertiliser in the soil-plant system over several years, helping to develop strategies to optimize its NUE and reduce nitrate leaching. We hypothesised that i) recovery of applied fertiliser N in plants is greater for mineral fertiliser than for cattle slurry, ii) a greater proportion of cattle slurry than mineral fertiliser N remains in the soil and therefore iii) cattle slurry has an elevated leaching potential over mineral fertiliser. At the same time, we expected iv) a higher residual fertiliser NUE for Slu than for Min.

2. Material and methods

2.1. Field site and experimental design

The field experiment was conducted as an on-farm trial on two field sites in the *Gäu* region, Canton Solothurn, Switzerland, between May 2018 and April 2020 (Field A) or July 2020 (Field B). It presents the continuation of Frick et al. (2022), and further details can be found therein. In brief, the two fields followed a shifted crop rotation with silage maize – winter wheat – grass-clover (Field A) and grass-clover – silage maize – winter wheat (Field B) (Fig. 1). Both fields had been cultivated with sown grass-clover for at least three years before the start of the experiment. During this time, they received animal manure three to four times per year according to common agricultural practice. Fields differed slightly in texture but were overall comparable in basic soil properties (Table 1). Bulk density, determined by cylinders in 0.05 m increments, was similar on both fields. Field A had a considerable stone content below 0.3 m, while at Field B, stone content below 0.3 m increased from east to west. Climatic conditions at the field site are temperate, with a mean annual temperature of 9.0 °C and a yearly precipitation of 1129 mm (1981–2010). However, weather conditions during 2018 and 2019 were characterised by abnormally hot and dry summer conditions (Fig. 2). The fields were not irrigated; the groundwater level is at about 6 m depth.

Three fertiliser treatments were implemented: ^{15}N labelled mineral fertiliser as $^{15}NH_4{}^{15}NO_3$ (Min, 8.00 atom% ^{15}N abundance), ^{15}N labelled cattle slurry (Slu, 7.89 atom% ^{15}N abundance), and a control treatment not receiving any ^{15}N labelled fertiliser (Con). Each fertiliser treatment was replicated four times, resulting in 12 microplots per field. On both fields, microplots were arranged in a complete randomised block design on a 3 m wide strip, 9 m apart from the edges of the fields. According to the design proposed by Jokela and Randall (1987), the unconfined microplots had a size of 1.5 m x 2 m and were located in a way that two maize rows formed the edges of each microplot and one maize row formed the centreline of the plot (0.75 m row spacing).

^{15}N labelled cattle slurry was produced by feeding a young heifer with ^{15}N labelled ryegrass for 8 days. Faeces and urine were sampled separately and frozen daily. Later, faeces and urine fractions with the highest ^{15}N label were recombined and diluted 1:1 with demineralised H_2O in order to achieve a representative slurry. The final slurry had a dry matter (DM) content of 34 g kg^{-1} fresh matter, a pH of 8.3, and contained total N (TN) = 67.8 g kg^{-1} DM, NH_4-N = 42.2 g kg^{-1} DM, and Corg = 393 g kg^{-1} DM. A fractionation into different N pools with differing recalcitrance revealed that the ^{15}N labelling was homogenous enough to use it as a quantitative tracer within this study. Further details on the production and characterisation of ^{15}N labelled slurry can be found in Frick et al. (2022).

2.2. Fertiliser application and microplot management

In 2018, both fields were fertilised with ^{15}N labelled fertilisers in amount and timing according to recommended agricultural practice.

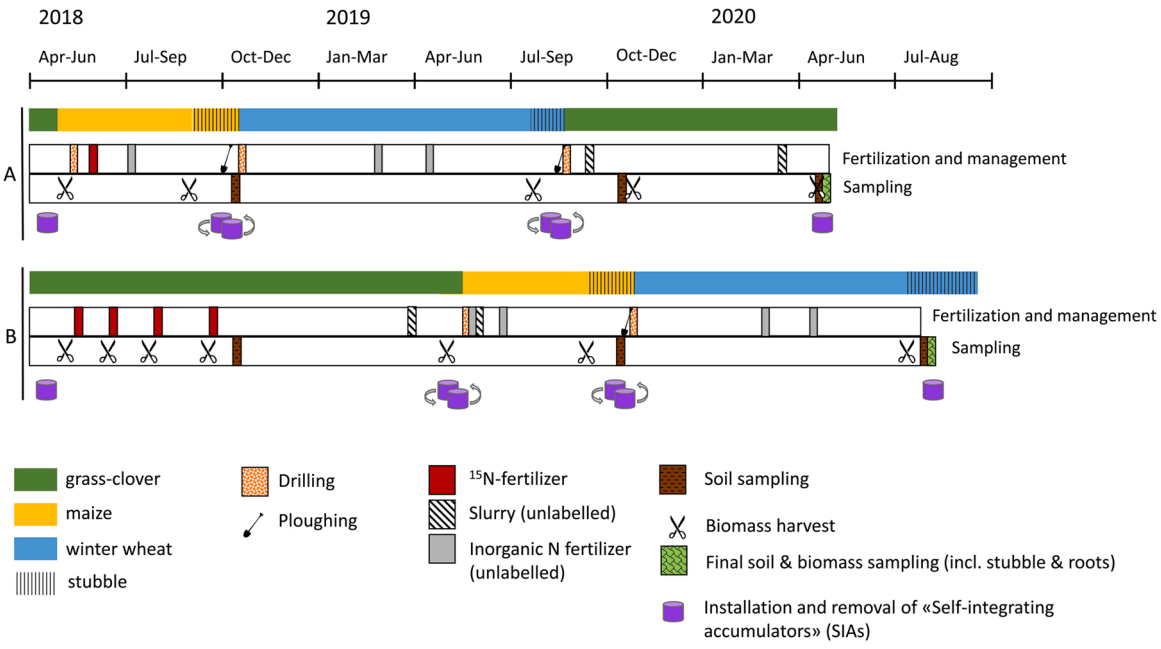

Fig. 1. Crop rotation, fertilisation and management as well as sampling scheme at the Field A (top) and Field B (bottom).

Table 1
Soil properties at the two field sites.

		Field A			Field B		
		0 – 0.3 m	0.3 – 0.6 m	0.6 – 0.9 m	0 – 0.3 m	0.3 – 0.6 m	0.6 – 0.9 m
Bulk density	[t m^{-3}]	1.40 ± 0.06	1.55 ± nd	nd	1.45 ± 0.04	1.57 ± 0.03	1.63 ± 0.02
Stone content[a]	[vol%]	5	30	40	0	0/20	10/50
pH ($CaCl_2$, 1:2.5)	[-]	5.5 ± 0.2	5.6 ± nd	5.6 ± nd	5.7 ± 0.2	5.8 ± 0.1	5.8 ± 0.1
C_{org}	g kg^{-1} DM	17.3 ± 0.4	10.1 ± 0.8	4.6 ± 0.4	17.8 ± 0.6	9.2 ± 1.5	5.4 ± 0.4
Total N	g kg^{-1} DM	1.9 ± 0.1	1.2 ± 0.1	0.6 ± 0.0	2.1 ± 0.3	1.0 ± 0.1	0.7 ± 0.1
Clay	[mass%]	22.0 ± 0.8	24.3 ± 0.9	26.3 ± 2.1	21.6 ± 1.0	22.3 ± 1.1	25.5 ± 0.5
Silt	[mass%]	35.8 ± 1.2	33.3 ± 1.8	23.9 ± 1.9	42.5 ± 1.5	42.9 ± 2.3	35.5 ± 4.3
Sand	[mass%]	39.6 ± 1.5	40.2 ± 1.8	49.0 ± 2.9	32.8 ± 0.6	33.2 ± 1.3	38.2 ± 3.9

[a] stone content was estimated visually in the field; at Field B, there was a gradient in the stone content below 0.3 m

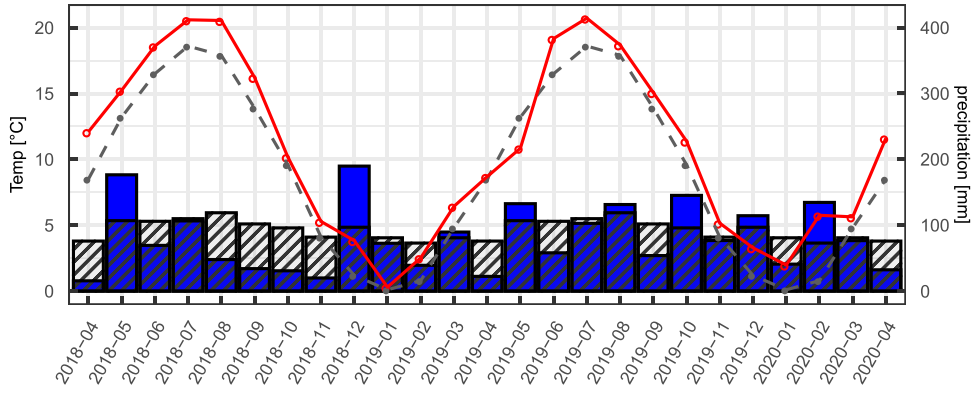

Fig. 2. Weather conditions at Wynau (closest meteorological station) during the time frame of the experiment. Monthly mean temperature [°C] is indicated in red (open circles), monthly sum of precipitation [mm] is indicated with blue bars. Grey dotted line and shaded bars show long-term average values (1981–2010).

On Field A, a single ^{15}N labelled fertiliser application was performed at the three to four leaf stage of silage maize. Slurry was applied to contain 60 kg N ha^{-1}, equivalent to 36.8 kg NH_4-N ha^{-1}, while ^{15}N mineral fertiliser solution was applied as ammonium nitrate at a rate equal to the NH_4-N-content of the slurry (i.e. 36.8 kg N ha^{-1}). Application was performed using canisters imitating drag hose application. On Con and Min microplots, additionally, phosphorus (P) (6.7 kg ha^{-1} P as triple super phosphate) and potassium (K) (75 kg ha^{-1} K as potassium sulphate) were applied to compensate for the amounts of these elements contained in the slurry. Also, the liquid added with the slurry was compensated by adding the same volume of water in the other treatments. During a later growth stage, non-labelled urea was applied to the whole field including all microplots (69 kg N ha^{-1}). Application of animal manure to an early growth stage of the maize in combination with

later N doses in the form of urea is a common practice in the region. Thus, we followed the fate of a single ^{15}N labelled fertiliser application.

On Field B, ^{15}N labelled fertilisers were applied after each cut of grass-clover during 2018, resulting in a total of four applications. The same amounts and procedure as for Field A were followed for each application.

Weed and pest control were performed by the farmer for the whole field including microplots. From 2019 on, also fertilisation was done by the farmer, using non-labelled fertilisers (Fig. 1, Table 2). Cultivation measures that involved soil movement such as ploughing after harvesting maize or winter wheat were conducted manually on the microplots.

2.3. Biomass and soil sample collection and preparation

Aboveground biomass of maize and wheat was harvested from the central area of the microplots, at least 0.375 m away from the microplot edged. Plants were cut manually upon maturity at about 0.01 m above the ground. Only the centre row on a length of 1.25 m (i.e. 0.75 m away for the plots` edge) was used for ^{15}N-analysis. The number of plants (maize) or the number of ears (winter wheat) from the central row were counted. Maize plants were split into stems, leaves, grain, and husk + cobs, while wheat plants were split into stems, grains and husk. All plant parts were dried at 60 °C and weighed. Additionally, the two adjacent rows were harvested and fresh weight as well as the number of plants (maize) or ears (winter wheat) were determined directly in the field and used for getting a more representative estimate of the dry matter yield compared to only determining the yield based on the central row. Furthermore, the rows at 0.75 m distance outside the microplots were sampled and processed as the central row. These samples were used to check for potential dilution of the ^{15}N label by unlabelled N from outside the microplot. Since these samples did not have any ^{15}N enrichment above the level in Con, we assumed that the ^{15}N values of plants in the central row, having the same distance from the plot edge as the outside row, can be considered undiluted from the outside and, thus, representative for N uptake solely from the area on which ^{15}N labelled fertilisers were applied.

For grass-clover, aboveground biomass was harvested with electric scissors from a 0.5 m x 0.5 m frame placed in the middle of each microplot ("inner frame"). Biomass was sorted into grass, legumes and other herbs, and dried at 40 °C. To get a more representative yield estimate, the harvesting area was increased to the whole central area of the microplot (1.25 m x 0.75 m, "outer frame") and total dry matter yield determined. It was assumed that the relative share of grass, legumes and herbs in the outer frame was the same as in the inner frame.

The final sampling at the end of the experiment included sampling of stubble and roots: For Field A, grass-clover stubbles were cut in the same 0.5 m x 0.5 m inner frame as the shoot biomass. Within this frame, soil was excavated in a 0.3 m x 0.2 m x 0.3 m cuboid, weighed and sieved through a 12 mm mesh in the field in order to quantify the amount of stones. Roots remaining on the sieve were collected and washed under running tap water in the laboratory. From the sieved soil, a subsample of approx. 1 kg was brought to the laboratory, where it was washed through a 1 mm sieve in order to quantify the amount of roots in the sieved soil. For this, the roots remaining on top of the sieve were separated from mineral debris and exogenous organic material by combined decantation and manual sorting with tweezers (Hirte et al., 2017). Roots were dried in the oven at 60 °C. Gravimetric soil water content was determined on a separate subsample. For Field B (winter wheat), a similar procedure was followed, with cutting and collecting the stubble from the three central rows of the microplot on a length of 1.25 m. Excavated soil from the centre of each microplot was treated as above in order to quantify and collect the roots.

Dried biomass samples were homogenised in a cutting mill, and a subsample was pulverised in a ball mill (MM200 Retsch, Haan, Germany) for later analysis of N content and ^{15}N enrichment.

Soil was sampled to a depth of 0.9 m at the end of each vegetation period, i.e. in mid-October in 2018 and 2019. In 2020, soil sampling was performed upon finalising the experiment, i.e. after harvest of grass-clover in April 2020 (Field A) and after harvest of winter wheat in July 2020 (Field B). Samples were taken as mixed samples, divided into 0.3 m increments, from three cores (0.02 m diameter) per plot taken with a distance of at least 0.375 m from the edge of the microplot. Samples were stored in cooling boxes on the field and at 4 °C after reaching the lab. Within 24 h, soil was sieved at 5 mm, and a subsample extracted with 0.5 M K_2SO_4, filtered through folded paper filters (Macherey Nagel Type 615, Ø 185 mm) and stored at − 20 °C until analysis for ammonium and nitrate. The remaining sieved soil was air-dried and pulverised for analysis of ^{15}N in the total N pool.

Table 2
N inputs over the duration of the experiment (details on management operations and other nutrient inputs can be found in SI A Table 1).

Field	Crop (Year)	Input type	N input amount
			kg N ha^{-1}
Field A	Maize (2018)	^{15}N fertiliser	0/36.8/60 for Con/Min/Slu
		Urea	69
	Winter wheat (2019)	Nitrophos	60
		Urea	92
	Grass-clover (2019/2020)	Cattle slurry	95 (of which 55 NH_4-N)
		Cattle slurry	95 (of which 55 NH_4-N)
Field B	Grass-clover (2018/2019)	^{15}N fertiliser (1st application)	0/36.8/60 for Con/Min/Slu
		^{15}N fertiliser (2nd application)	0/36.8/60 for Con/Min/Slu
		^{15}N fertiliser (3rd application)	0/36.8/60 for Con/Min/Slu
		^{15}N fertiliser (4th application)	0/36.8/60 for Con/Min/Slu
		Cattle slurry (spring)	95 (of which 55 NH_4-N)
	Maize (2019)	NPK	30
		Cattle slurry	76 (of which 44 NH_4-N)
		Urea	92
	Winter wheat (2020)	Nitrophos	40
		Urea	69

2.4. Measuring nitrate leaching with self-integrating accumulators

Nitrate leaching was assessed cumulatively per growing-season using so-called self-integrating accumulators (SIAs) (Bischoff, 2007; Grunwald et al., 2020; Wey et al., 2022). In short, SIAs are patented passive samplers, consisting of PVC-tubes (diameter = height = 0.1 m) filled with an ion-exchange-resin-sand mixture collecting leached nitrate and ammonium (TerrAquat Consultants; patent no. 197 26 813). Three SIAs per microplot were installed at 1 m depth in horizontal access tunnels in order to place the SIAs underneath the undisturbed soil profile. SIAs were regularly exchanged after harvesting each crop (Fig. 1). After removing the SIAs, the sand-resin mix was split into three layers and the material was well mixed within each layer. Both the uppermost layer (0 – 0.05 m) and the middle layer (0.05 – 0.06 m) were extracted with 1 mol L^{-1} NaCl solution for analysis of ammonium and nitrate. Thereby, the uppermost layer is supposed to hold all leached nitrate and ammonium, while the middle layer is used to check for the validity of this assumption. For analysing ^{15}N enrichment in nitrate, extracts were diffused on acidified glass fibre discs. First, 200 mg MgO were added for the diffusion of ammonium during 72 h shaking and afterwards 400 mg Devarda`s alloy was added to the same sample and again shaken for 72 h for the sequential diffusion of nitrate on a separate filter disc (Goerges and Dittert, 1998).

2.5. Laboratory analysis of slurry, soil and biomass samples

Total N, NH_4-N, P and K content of the slurry were analysed on the fresh slurry at the laboratory for soil and environmental analysis (LBU, Eric Schweizer AG, Steffisburg, Switzerland).

Soil and SIA extracts were analysed colorimetrically for nitrate and ammonium: Nitrate content of the extracts was determined according to Keeney and Nelson (1982), while ammonium, both in soil and SIA extracts, was determined using the modified indophenol blue reaction (Krom, 1980). Both analyses were performed on an automated discrete analyser (Smartchem 450 Discrete Analyser, AMS Alliance).

All total N and ^{15}N analyses (soil, biomass, diffusion filters) were performed on an elemental analyser coupled with a continuous flow isotope ratio mass spectrometer (Pyro cube + isoprime100, Elementar, Germany). International standards (IAEA-N1, IAEA-N2) and internal references were included as quality check in each analysis run.

2.6. Calculations

For all ^{15}N data, isotopic excess was calculated by subtracting the mean ^{15}N abundance (i.e. percentage of ^{15}N relative to total N) of non-labelled reference samples from the measured ^{15}N abundance. For the mineral fertiliser, the natural abundance of ^{15}N in air was subtracted as a reference (i.e. 0.3663 atom%), while for slurry the weighted mean ^{15}N abundance of non-labelled faeces and urine samples from the same animal was used as non-labelled reference (0.386 atom%) (Frick et al., 2022). For plant biomass or SIA extracts, the mean of the Con treatment at the corresponding sampling time in the corresponding sample type (plant, soil, extracts) was used as a reference.

The ^{15}N excess was used to calculate the proportion of N derived from fertiliser (Ndff) in the samples (Hauck and Bremner, 1976):

$$Ndff_{rel}\ [\%] = \frac{atom\%\ ^{15}Nexcess\ sample}{atom\%\ ^{15}Nexcess\ fertilizer} \times 100 \quad (1)$$

where atom% ^{15}Nexcess sample is the ^{15}N enrichment of the considered compartment (i.e. plant (part), soil, extracts) and atom% ^{15}Nexcess fertiliser refers to the ^{15}N enrichment of either mineral fertiliser or slurry (see 2.1).

The amount of N derived from the fertiliser was calculated as:

$$Ndff\quad \left[kg\quad ha^{-1}\right] = \frac{Ndff_{rel}\quad [\%]}{100} \times TN_i \quad (2)$$

where TN_i is the total amount of N in the considered compartment expressed in kg N ha^{-1}. TN_i was calculated from the N concentration in the compartment multiplied with its dry weight in kg ha^{-1}. The mass of the soil per layer was determined by multiplying its volume with the bulk density (Table 1).

N derived from other sources (Ndfo) such as soil, unlabelled fertiliser or deposition was determined as the difference between total N uptake and Ndff, or when grass-clover was grown, between N uptake and the sum of Ndff and N from biological N fixation by clover (Nfix). For Slu and Min, Nfix was calculated by the ^{15}N enriched dilution method (Mcauliffe et al., 1958), while for Con, Nfix was calculated by the natural abundance method (Shearer and Kohl, 1986). Further details can be found in (Frick et al., 2022).

The recovery of the applied fertiliser in the different compartments was calculated as:

$$recovery[\%] = \frac{Ndff}{N_{applied}} \times 100 \quad (3)$$

where $N_{applied}$ is the total amount of N applied with the labelled fertiliser.

Leached nitrate collected in SIAs was calculated as follows:

$$NO_3\quad \left[kg\quad N\quad ha^{-1}\right] = \frac{NO_{3resin} \times weight_{resin}}{area_{SIA}} \quad (4)$$

where NO_{3_resin} is the NO_3-N amount in the resin [kg N kg^{-1} resin], $weight_{resin}$ is the total weight of the adsorber resin material in the SIA, and $area_{SIA}$ is the surface area of the SIA.

For statistical analysis and data visualisation, mean values of the three replicated SIAs per microplot were used. However, nitrate concentration was too low for reliable ^{15}N determination in eleven SIAs and one SIA was lost upon excavation. Therefore, mean values were based on only two replicates in five out of 72 cases and on one replicate in two cases. For one microplot in 2018, no reliable data could be obtained.

Cumulative recovery in harvested biomass, nitrate leaching, as well as recovery in soil, roots and stubble upon the final sampling were summed up in order to assess the fate of the labelled fertilisers in the soil-plant-system over the duration of the experiment. To complement the balance, NH_3 emission upon application of the fertilisers in the first year were included (Frick et al., 2022).

In order to assess the availability of the residual fertiliser N left in the system after harvest of crops present in the application year or in the first year after application, residual recovery in 2019 and 2020 was calculated by two different approaches: In the first approach, residual recovery was calculated relative to the measured amount of ^{15}N labelled fertiliser left in soil (compare method 3 in Smith and Chalk, 2018):

$$residual\quad recovery_{soil}[\%] = \frac{Ndff_{crop}}{Ndff_{soil}} \times 100 \quad (5)$$

with $Ndff_{crop}$ denoting Ndff in crop in the residual years and $Ndff_{soil}$ denoting Ndff in soil (0 – 0.9 m) in October of the preceding year, thus, residual fertiliser N in soil. Both are given in kg N ha^{-1}.

With this approach, however, ^{15}N in the stubbles and roots of the pre-crop, which might be mineralised and become plant available later, is not taken into account. Thus, we applied an additional approach:

$$residual\quad recovery_{output}[\%] = \frac{Ndff_{crop}}{N_{applied} - Ndff_{precrop(s)} - Ndff_{leaching} - NH_3} \times 100 \quad (6)$$

where $Ndff_{crop}$ is Ndff in crop, $N_{applied}$ is the amount of labelled N applied in 2018, $Ndff_{precrop(s)}$ is Ndff amount harvested with above-ground biomass of the preceding crop(s), $Ndff_{leaching}$ is Ndff collected in leached nitrate of the preceding year(s) and NH_3 is the mean amount of NH_3-N volatilised upon application of the fertilisers in 2018.

2.7. Statistical analysis

Data preparation and statistical analysis were performed using R (Version 3.5.3) (R Core Team, 2019). A significance level of $p < 0.05$ was applied throughout. Statistical analyses were performed separately for the two fields using mixed effect linear models (lmer within package *lme4*). Throughout, model validation was performed by qq-plotting. *emmeans*-package was used for pairwise comparisons. p-value adjustment for multiple comparisons was performed according to the Tukey-method.

For biomass yield, TN uptake, Ndff and recovery, analyses were performed separately for each year and included *treatment* as fixed effect and *block* as random effect. For recovery, log-transformed data were used.

For assessing statistically significant differences between the fertilisers in terms of depth translocation in soil over the years, separate mixed effect linear models were fitted for recovery and Ndff in soil, with *depth*, *year* and *treatment* as well as their two-way interactions as fixed effects. To account for repeated measurements with time and the non-independent structure of the different depth layers, *microplot*, *year*:

microplot and *block* were introduced as random factors. Analyses were performed on log-transformed data. Since measurements in the 0.6 – 0.9 m depth layer in 2018 were close to the quantification limit resulting negative values had to be excluded from statistical analysis (concerned n = 6 for Field A, n = 2 for Field B). However, for calculations of the residual recovery$_{soil}$ and within figures, negative values were replaced by 0.

For nitrate leaching, including Ndff and recovery in leached nitrate, *microplot* as well as *block* were used as random effects to account for repeated measurements. *Treatment* and *year* as well as their interaction were included as fixed effects in the mixed effect linear models. In addition, cumulated values for nitrate leaching, Ndff in nitrate and recovery over the three sampling periods were compared between the fields considering *treatment, field* and their interaction as fixed effects and *block* as random effect. Log-transformed data were used, except for cumulated nitrate leaching and Ndff, where non-transformed data could be used.

Usually missing values were excluded from statistical analysis. This concerned two missing values upon biomass sampling at Field A in 2019, caused by game damage, and one missing value for nitrate leaching, because concentration was too low for ^{15}N determination (see above). To calculate the overall balance and *residual recovery$_{output}$*, however, we replaced missing values by the mean of the other replicates per treatment and field.

3. Results

3.1. N use efficiency in crops

Dry matter yield and N uptake were generally similar for all fertiliser treatments throughout the experiment, except for greater yields of grass-clover in Slu at Field A in 2019/2020, and lower yields in Con at Field B in 2018/19. N uptake was slightly but significantly greater for Slu than for the other treatments in maize (2018) and in grass-clover (2019/20) at Field A (Table 3). Dry matter yield levels for the different crops were similar between the two fields. However, N uptake for both maize and wheat on Field A was lower than values obtained in the succeeding year at Field B.

In contrast to total N uptake and dry matter yield, Ndff was about 1.3-times higher for Min than for Slu in 2018, both at Field A ($p = 0.004$) and Field B ($p = 0.028$) (Table 3). In the year of application, plants took up 11.7% (Field A) or 23.3% (Field B) of their N demand from ^{15}N labelled mineral fertiliser. For Slu, these shares amounted to 7.7% at Field A and 19.3% at Field B. In the following two years, Ndff$_{rel}$ declined to less than 1.5% (Field A) or less than 5% (Field B) of plant N uptake. Thereby, differences in absolute amounts of Ndff were always statistically significant between the two fertiliser treatments, but in contrast to the first year, Ndff for Slu was higher than Ndff for Min (Table 3).

Relative to the total amounts of ^{15}N labelled mineral fertiliser applied in 2018, harvested plant biomass recovered 44.7 – 47.1% in 2018, 3.6 – 3.9% in 2019 and 1.6 – 1.7% in 2020. For Slu, recoveries in biomass amounted to 19.2 – 23.1% in 2018, 4.2 – 4.6% in 2019 and 1.9 – 2.4% in 2020 (Table 4). Thereby, differences between Min and Slu were small, but statistically significant except for Field A in 2019.

Upon finalising the experiment, also root and stubble biomass and their ^{15}N contents were assessed. For Field A, shoot biomass of the final grass-clover cut in April 2020 (2.5 – 2.9 t ha^{-1}), stubble and root each yielded about the same amount of dry matter (**SI B** Table 1). Recovery of originally applied fertiliser N was < 0.8% in roots and < 0.6% in stubble. For Field B, combined root plus stubble biomass amounted to about 17% of harvested aboveground biomass of wheat, and ^{15}N fertiliser amounts recovered in stubble and roots were negligible (< 0.5%) (Fig. 3).

3.2. Fertiliser recovery in soil

Throughout the experiment, fertiliser recovery in different soil depth layers showed a similar distribution for both fields (Fig. 4). Most fertiliser N was recovered in the top 0.3 m for both fertilisers and both fields. Recovery tended to be greater for Slu than for Min, with differences being significant in 2018 and 2020 on Field A and in 2020 on Field B. Upon the final sampling in 2020, 44–52% of applied slurry N was still recovered in topsoil, compared to 20–23% of the mineral fertiliser applied in 2018.

Only minor shares of mineral fertiliser or slurry N were translocated into deeper soil layers during the 2.5 years duration of this experiment. At Field A, recovery of labelled N in deeper soil layers was negligible in

Table 3
Total dry matter yield, N uptake and source of N uptake for the three crops at the two fields during 2018 – 2020; mean ± standard deviation; n = 4 (except Field B Maize 2019 Min and Slu n = 3); Ndff = N derived from fertiliser, Nfix = N from biological nitrogen fixation by clover; Ndfo = N derived from other sources such as soil N, deposition, unlabelled fertiliser N. Different letters indicate statistically significant difference between the treatments within the same crop at $p < 0.05$.

Field	Crop (Year)	Treatment	Yield	N uptake	Ndff	Nfix[a]	Ndfo
			t ha^{-1}	kg N ha^{-1}			
Field A	Maize (2018)	Con	16.4 ± 0.6 ^{ns}	137.3 ± 9.9^{a}	–	–	137.3 ± 9.9^{a}
		Min	17.9 ± 0.9 ^{ns}	140.3 ± 4.5^{a}	16.4 ± 0.9^{a}	–	123.9 ± 5.1^{b}
		Slu	17.6 ± 1.0 ^{ns}	149.7 ± 4.9^{b}	11.5 ± 1.0^{b}	–	138.2 ± 4.8^{a}
	Winter wheat (2019)	Con	12.9 ± 1.1 ^{ns}	192.2 ± 17.5 ^{ns}	–	–	192.2 ± 17.5 ^{ns}
		Min	12.5 ± 1.4 ^{ns}	182.8 ± 18.1 ^{ns}	1.3 ± 0.1^{a}	–	181.5 ± 18.0 ^{ns}
		Slu	12.3 ± 0.4 ^{ns}	192.9 ± 14.3 ^{ns}	2.5 ± 0.1^{b}	–	190.3 ± 14.3 ^{ns}
	Grass-clover (2019/2020)[b]	Con	4.6 ± 0.2^{a}	129.7 ± 10.3^{ab}	–	27.9 ± 13.8 ^{ns}	101.7 ± 7.0^{a}
		Min	4.4 ± 0.1^{a}	117.8 ± 1.9^{a}	0.6 ± 0.1^{a}	14.3 ± 4.9 ^{ns}	102.9 ± 6.1^{ab}
		Slu	5.1 ± 0.4^{b}	143.5 ± 10.5^{b}	1.5 ± 0.3^{b}	17.1 ± 15.8 ^{ns}	125.0 ± 17.4^{b}
Field B	Grass-clover (2018/2019)[c]	Con	9.6 ± 0.6^{a}	254.2 ± 36.0 ^{ns}	–	43.1 ± 28.5 ^{ns}	211.1 ± 9.5 ^{ns}
		Min	11.6 ± 0.5^{b}	297.3 ± 21.9 ^{ns}	69.4 ± 7.4^{a}	19.0 ± 15.6 ^{ns}	208.9 ± 23.1 ^{ns}
		Slu	11.4 ± 0.8^{b}	287.4 ± 27.9 ^{ns}	55.4 ± 1.4^{b}	14.2 ± 10.2 ^{ns}	217.8 ± 26.3 ^{ns}
	Maize (2019)	Con	18.4 ± 1.6 ^{ns}	194.9 ± 17.5 ^{ns}	–	–	194.9 ± 17.5 ^{ns}
		Min	18.5 ± 0.5 ^{ns}	192.6 ± 1.5 ^{ns}	5.7 ± 0.1^{a}	–	186.9 ± 1.5 ^{ns}
		Slu	19.8 ± 0.8 ^{ns}	211.0 ± 23.8 ^{ns}	11.1 ± 1.3^{b}	–	200.0 ± 22.7 ^{ns}
	Winter wheat (2020)	Con	12.4 ± 0.6 ^{ns}	220.5 ± 19.7 ^{ns}	–	–	220.5 ± 19.7 ^{ns}
		Min	12.3 ± 0.9 ^{ns}	222.8 ± 16.9 ^{ns}	2.4 ± 0.3^{a}	–	220.4 ± 16.6 ^{ns}
		Slu	12.4 ± 1.1 ^{ns}	221.0 ± 21.5 ^{ns}	4.6 ± 0.6^{b}	–	216.3 ± 21.2 ^{ns}

[a] For Min and Slu, Nfix was calculated by the ^{15}N enriched dilution method (Mcauliffe et al., 1958), while Nfix of Con was calculated by the natural abundance method (Shearer and Kohl, 1986)
[b] Grass-clover data refers to cumulated values over two cuts between Sep 2019 and Apr 2020
[c] Grass-clover data refers to cumulated values over four cuts between Jun 2018 and Apr 2019

Table 4
Recovery and residual fertiliser recovery in crop biomass. Recovery is expressed relative to the originally applied amount of ^{15}N fertiliser. Residual $recovery_{soil}$ refers to the recovery based on residual ^{15}N amount measured in soil (0 – 0.9 m) in October of the preceding year. Residual $recovery_{output}$ refers to the recovery of calculated residual ^{15}N left in the system after considering N uptake by pre-crop (s) and losses via NO_3 leaching and NH_3. mean ± standard deviation; n = 4 (except Field B Maize 2019 Min and Slu n = 3). Different letters indicate statistically significant differences between the treatments within the same crop at $p < 0.05$.

Field	Crop (Year)	Treatment	Recovery	Residual $recovery_{soil}$	Residual $recovery_{output}$
			%		
Field A	Maize (2018)	Min	44.7 ± 2.6[a]	–	–
		Slu	19.2 ± 1.7[b]	–	–
	Winter wheat (2019)	Min	3.6 ± 0.4 [ns]	13.0 ± 2.6[a]	6.7 ± 1.1 [ns]
		Slu	4.2 ± 0.2 [ns]	7.6 ± 2.0[b]	5.8 ± 0.2 [ns]
	Grass-clover (2019/2020)[a]	Min	1.7 ± 0.3[a]	3.8 ± 1.1 [ns]	3.7 ± 1.2 [ns]
		Slu	2.4 ± 0.5[b]	5.0 ± 1.1 [ns]	3.9 ± 0.6 [ns]
Field B	Grass-clover (2018/2019)[b]	Min	47.1 ± 5.0[a]	–	–
		Slu	23.1 ± 0.6[b]	–	–
	Maize (2019)	Min	3.9 ± 0.0[a]	10.8[c] ± 2.6 [ns]	8.0 ± 0.9 [ns]
		Slu	4.6 ± 0.5[b]	8.1[c] ± 2.4 [ns]	7.1 ± 0.7 [ns]
	Winter wheat (2020)	Min	1.6 ± 0.2[a]	4.2 ± 0.7 [ns]	3.6 ± 0.4 [ns]
		Slu	1.9 ± 0.2[b]	3.0 ± 0.4 [ns]	3.2 ± 0.4 [ns]

[a] Grass-clover data refers to cumulated values over two cuts between Sep 2019 and Apr 2020

[b] Grass-clover data refers to cumulated values over four cuts between Jun 2018 and Apr 2019

[c] Note: With grass-clover as pre-crop, residual $recovery_{soil}$ might be underestimated as soil samples were always taken in October of the preceding year, neglecting the overwintering grass-clover. If ^{15}N taken up by overwintering grass-clover is considered, residual $recovery_{soil}$ in maize 2019 would increase from 10.8% to 12.2% for Min and from 8.1% to 8.8% for Slu.

2018, but increased to 6 – 8% in 2019 ($p < 0.0001$). At Field B, already in the first year, 5 – 6% of both Slu and Min was translocated to the 0.3 – 0.6 m layer, but except a significant increase in the 0.6 – 0.9 m layer from 2018 to 2019 in Slu, further increases over the years in the deeper soil layers were not significant and similar between the two treatments. However, a slightly higher share of Slu compared to Min was recovered in the 0.3 – 0.6 m layer in 2020 ($p = 0.03$).

In contrast to the relative recovery based on the originally applied fertiliser N, absolute amounts of residual fertiliser N in soil showed clear differences between the fertiliser treatments, with Ndff for Slu two to three times higher than for Min (**SI B** Fig. 1). Again, depth translocation was minor and on average less than 2 kg N (Field A) or less than 10 kg N (Field B) from the labelled fertilisers were found below 0.6 m depth in 2020. Differences between years were small, but at Field A, the increase from 2018 to 2019 in Ndff in the soil layers below 0.3 m was highly significant for both Min and Slu ($p < 0.001$). For Field B, only the increase from 2018 to 2019 in the 0.9 m depth layer was significant for Slu ($p = 0.04$).

3.3. Nitrate leaching from ^{15}N labelled fertilisers

Nitrate leaching did not differ between treatments, but there was a highly significant effect of the leaching period ($p < 0.001$). Thereby, the highest leaching under both fields was found under winter wheat, with values ranging between 73 and 106 kg NO_3-N ha^{-1} at Field A (2019) and between 128 and 194 kg NO_3-N ha^{-1} at Field B (2020) (Fig. 5). High nitrate leaching coincided with high nitrate levels in soil in October of the preceding year (SI B Fig. 2).

The amount of nitrate leached from ^{15}N labelled fertilisers was low. At both fields, Ndff in leached nitrate underneath winter wheat was significantly higher than underneath the other crops. During this time, more slurry N (for Field A in 2019: 3.5 kg N ha^{-1}, for Field B in 2020: 6.9 kg N ha^{-1}) than mineral fertiliser N (for Field A in 2019: 1.5 kg N ha^{-1}, for Field B in 2020: 3.5 kg N ha^{-1}) was leached, but these differences were not significant (Fig. 5).

Cumulated over the three vegetation periods, NO_3^- leaching did not differ between the two fields nor between the three fertiliser treatments, averaging 119 – 205 kg NO_3-N ha^{-1} (Fig. 5). Of this amount, 2–8 kg NO_3-N ha^{-1} originated from the ^{15}N labelled fertilisers. The absolute amount of fertiliser N lost via nitrate leaching was higher for Slu than for Min ($p < 0.001$), and higher for Field B than for Field A ($p = 0.004$). Summarised over both fields, for Slu > 95% and for Min > 98% of leached nitrate did not originate from ^{15}N labelled fertilisers applied in 2018. Recovery of ^{15}N labelled fertilisers in leached nitrate was significantly higher ($p = 0.003$) for the single ^{15}N labelled fertiliser application to maize at Field A (6.3–7.7%) than for the repeated applications to grass-clover at Field B (2.5–3.2% of applied ^{15}N labelled fertiliser), but there were no differences between Min and Slu.

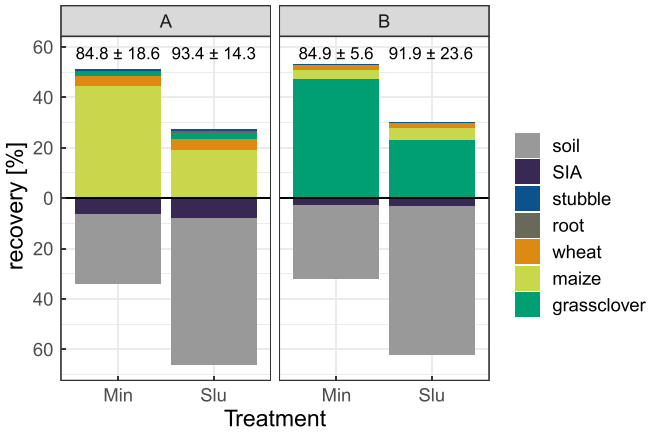

Fig. 3. Recovery of ^{15}N labelled fertilisers over the years 2018, 2019 and 2020 at Field A (left) and Field B (right). For aboveground biomass, data is shown separately for the individual crops. For nitrate leaching collected in self-integrating accumulators (SIAs), data is shown cumulated over the three years. For stubble, roots and soil (0 – 0.9 m), data from the final sampling in 2020 were used. Numbers on top indicate overall recovery in all measured compartments (mean ± standard deviation, n = 4). Note: ammonia emission were recorded within Frick et al. (2022) and amounted to ~0% for Min and 6.6% for Slu at Field A, and to 3.4% for Min and 10.1% for Slu at Field B, relative to the applied amounts.

3.4. Residual fertiliser value of cattle slurry and mineral fertiliser

Higher proportions of applied ^{15}N slurry than ^{15}N mineral fertiliser were recovered in crop biomass in the two residual years. However, when considering only the amounts of ^{15}N fertilisers left in the soil or soil-plant system after harvest of the preceding crop(s), residual recovery of mineral fertiliser and slurry showed no differences (Table 4). In the first residual year (2019), residual recovery ranged between 5.8% and 13% of the remaining fertiliser in the soil, while it ranged between 3% and 5% in the second residual year (2020). It must be noted that estimates based on the ^{15}N measured in the soil in October of the preceding year (compare Eq. 5) tended to be slightly higher and more variable than values based on the calculated residual fertiliser amount

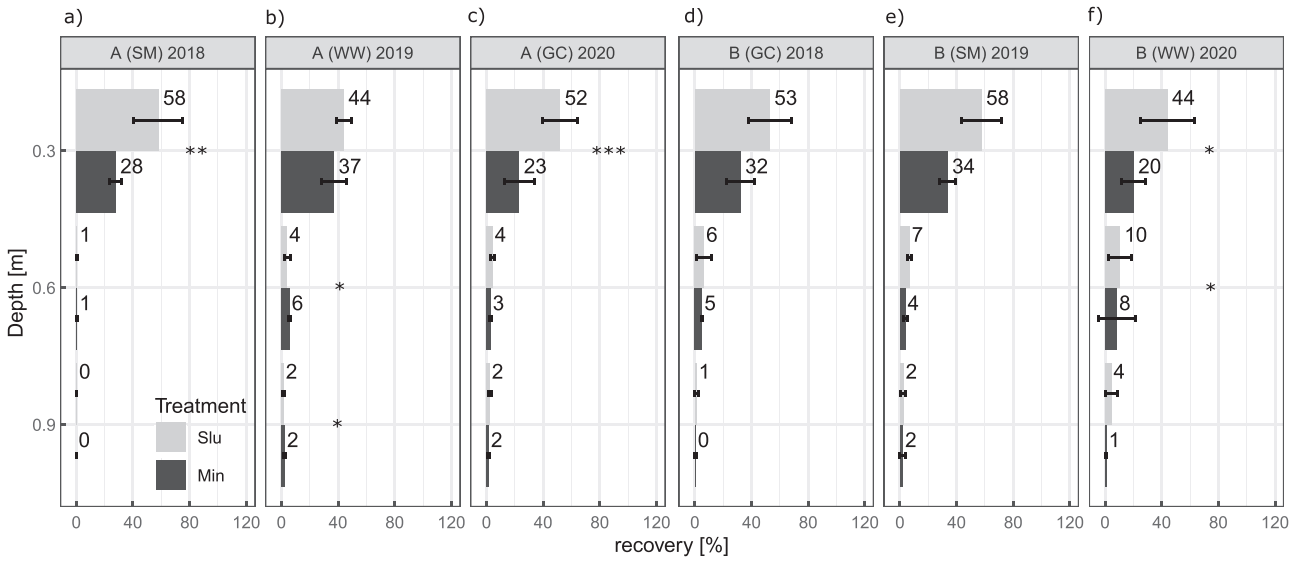

Fig. 4. ^{15}N recovery in soil relative to originally applied fertiliser for Field A (a-c) and for Field B (d-f). Samples in 2018 and 2019 were taken at the end of the vegetation period in mid-October, while sampling in 2020 took place upon harvest of the grass-clover in April (Field A) or upon harvest of winter wheat in July (Field B). SM = silage maize, WW = winter wheat, GC = grass-clover mean ± standard deviation, n = 4, with * ($p < 0.05$), * * ($p < 0.01$), and * ** ($p < 0.001$).

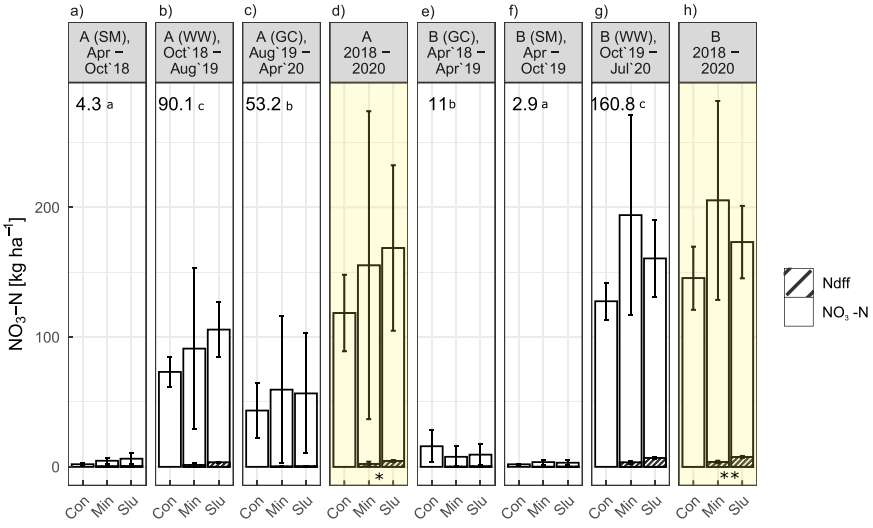

Fig. 5. Nitrate leaching measured with self-integrating accumulators (SIAs) at Field A (a – c) and at Field B (e – g) during three consecutive leaching periods. Cumulated values over the whole time frame are indicated in d) and h). n = 4, mean ± standard deviation; SM = silage maize, WW = winter wheat, GC = grass-clover; Ndff = N derived from fertiliser; numbers on top show average nitrate leaching at the individual leaching periods. Within each field, numbers followed by different letters are significantly different at $p < 0.05$. Statistically significant differences between Min and Slu in Ndff are indicated with * ($p < 0.05$) and * * ($p < 0.01$). For total NO_3-N leaching there were no statistically significant difference.

considering losses and plant uptake (compare Eq. 6).

3.5. ^{15}N soil-system balance over three cropping seasons

Upon the end of the experiment, cumulative recovery of originally applied fertiliser N in plants, leached nitrate, soil, stubble and roots, together with NH_3 emissions, should sum up to approximately 100%. For Min, we recovered about 85% of applied fertiliser N in the measured compartments, with NH_3 losses adding up to 3% of the applied amounts (Fig. 3). For Slu, total recovery reached 92–93%, with NH_3 emissions adding 7–10%. Cumulative recoveries obtained on the two fields showed high accordance. Despite similar cumulative recoveries, the distribution between aboveground and belowground recoveries differed between Min and Slu, with higher recovery of Min in plants and higher recovery of Slu in soil.

4. Discussion

4.1. Nitrogen use efficiency in crops greater for mineral fertiliser than for cattle slurry

Recovery of ^{15}N labelled mineral fertiliser in aboveground biomass of the first crop was about double the recovery of slurry N at both field sites (Table 4). This is in accordance with our hypothesis and was also reported by others (Bosshard et al., 2009; Thomsen et al., 1997). This can partly be explained by the fact that the applied amount of total N was about 1.6 times higher for Slu than for Min, since the same amount of mineral N was applied with both fertilisers. At the same amount of N derived from fertiliser, recovery, as a proportion of total N applied N, would therefore be lower for Slu than for Min (Eq. 3). However, even Ndff was significantly higher for Min than for Slu in the first year (Table 3). This contradicts results by Bosshard et al. (2009), but it indicates that mineral N within slurry was less available for plants, as also found by others (Sørensen, 2004). This results from a combination of higher NH_3 volatilisation from Slu than from Min and higher microbial

immobilisation of ammonium N from slurry in soil due to simultaneous addition of organic material with the slurry (Frick et al., 2022; Gutser and Dosch, 1996).

Differences in biomass yield and N uptake between the treatments were small or absent (Table 3). This can be explained by the overall small differences in N inputs between the treatments and by the additional non-labelled fertilisers applied by the farmer (Table 2). Furthermore, both fields had been cultivated with grass-clover for at least three years before commencement of the experiment, receiving three to four applications of cattle slurry per year. Thus, soils presumably had a high mineralisation potential of accumulated N.

Recoveries in aboveground biomass in the subsequent years were similar for both fertilised treatments (Table 4) and fell in the range of values reported in the literature (e.g. Smith and Chalk, 2018). Despite considerable biomass production by roots and stubble, fertiliser recovery in these plant parts at the end of the experiment was low and therefore contributed marginally to the cumulative recovery of fertiliser N in the soil-plant-system (SI B Table 1).

4.2. Persistently high fertiliser recoveries in soil

Complementary to greater fertiliser recovery in crops for Min than Slu, we anticipated that more slurry N than mineral fertiliser N would remain in soil. This was indeed the case, although differences were mostly not significant (Fig. 4). Overall, ^{15}N amounts recovered in 0 – 0.3 m depth (Min 20 – 37%, Slu 44 – 58%) were comparable to results obtained by others (Sørensen, 2004; Muñoz et al., 2003). We did not observe major changes over time in the ^{15}N recovered in the different depth layers for either fertiliser (Fig. 4). Similarly, in a 3-year field study, Muñoz et al. (2003) found the recovery of animal manure in the 0 – 0.3 m depth layer to persist at > 82% of total ^{15}N recovered in soil down to 0.9 m depth. Changes could have been expected due to a) plant N uptake, b) losses via nitrate leaching, or c) losses as N_2O or N_2 emissions from nitrification or denitrification. In our study, both plant N uptake of residual fertiliser N and nitrate leaching happened only to a minor extent (Table 4 and Fig. 5). Denitrification losses via N_2O, despite their relevance for climate change, only concern about 1% of applied fertiliser N (IPCC, 2006) and are therefore only a minor loss pathway. N_2 losses can be substantially higher than N_2O losses, but are hard to quantify and likely did not play a major role in our study as suggested by the continued high recovery of fertiliser N in the soil. Fluctuations, especially in topsoil, were likely due to mineralisation of ^{15}N that had been previously incorporated in plant roots or stubble (Hoekstra et al., 2011). In our study, these plant parts were only sampled at the end of the experiment.

The fact that about a fifth to a quarter of the mineral fertiliser N and about half of cattle slurry N remained in the soil even after the third vegetation period (Fig. 4) could hint towards N accumulation in the soil, especially considering that arable fields are usually regularly fertilised with both mineral fertiliser and manures. However, with increased N stocks under continuous inputs, also mineralisation-immobilisation turnover and potential nitrification rates were shown to be increased (Luxhøi et al., 2004; Luxhøi et al., 2007). We found that plants took up most of their N demand from sources other than the labelled fertilisers, even in the first year (Table 3). It can be assumed that most of it originated from mineralisation of soil N. Since plants in Min had higher Ndff values in the first year than those in Slu, plants fertilised with slurry needed to take up more N from soil to reach the same levels of total N uptake. The observed higher amount of slurry-N remaining in soil, indicates an enhanced restocking of soil N reserves and a potential long-term supply over the level of mineral fertiliser. This was confirmed by higher Ndff values in crop biomass for Slu than for Min in the two residual years (Table 3).

Nevertheless, it remains challenging to predict the long-term development of soil N levels under continuous fertilisation, and there is no consensus on the differential effect of repeatedly applied animal manure versus mineral fertiliser. Mulvaney et al. (2009) argue that mineral N fertilisers deplete soil N by increased mineralisation due to a lowered C: N ratio, but this has been questioned by others (Powlson et al., 2010; Glendining et al., 1996). Edmeades (2003) reported increased organic matter with long-term manure application. At the same time, there is concern about declining soil organic matter (SOM) and declining soil N stocks under cultivated land, and it was shown that manure application could just barely compensate for it (Ladha et al., 2011; Bosshard, 2007). This is also emphasised by the fact that total N outputs (plant N uptake + nitrate leaching losses) exceeded N inputs with fertilisers (both labelled and unlabelled) by 149 – 184 kg N (Field A) or 250 – 413 kg N (Field B) over the whole experimental crop rotation (Table 2, Table 3, Fig. 5).

Protection of N inputs in aggregates and distribution over different SOM fractions play an important role in understanding the fate of residual mineral fertiliser and slurry. Bosshard et al. (2008) found most ^{15}N in soil recovered in the mineral associated organic matter fraction (MAOM), irrespective whether it originated from ^{15}N mineral fertiliser or ^{15}N sheep faeces. Thereby, MAOM was assumed to have a low turnover rate, potentially explaining the observed low residual fertiliser effect (Table 4). However, recent evidence suggests that also N from MAOM gets plant available (Daly et al., 2021; Jilling et al., 2018). Furthermore, Bosshard et al. (2008) showed that upon experimental fractionation, a substantial amount of N was lost, confirming the importance of aggregates to protect SOM and highlighting the potential effect of soil tillage on re-mineralisation and potential loss of stabilised fertiliser N in soil. We could confirm this observation as we found the highest mineral N release after termination of grass-clover, as indicated by increased levels of nitrate in soil as well as elevated nitrate leaching (compare 4.4, SI B Fig. 2, Fig. 5).

4.3. Minor nitrate leaching from recently added fertilisers

We had expected greater nitrate leaching from cattle slurry than mineral fertiliser due to the combination of greater total N input, more residual N remaining in the soil and increased mineralisation-immobilisation turnover. In terms of total nitrate leaching, we did not observe differences between the fertilised treatments nor to the unfertilised control (Fig. 5). This can be attributed to the small differences in N inputs between the treatments and is in accordance with the insignificant differences in total N uptake by plants. In agreement with our hypothesis, cumulated nitrate leaching from slurry N was indeed higher than from mineral fertiliser N. This supports suggestions by others (e.g. Sørensen, 2004, Thomsen et al., 1997, Gutser and Dosch, 1996) that greater accumulation of manure N in soil increases nitrate leaching. However, the amounts of labelled fertiliser N that were leached were small for both Min and Slu. This is in accordance with several other studies finding that newly added fertiliser N barely gets leached (Glendining et al., 1996; Glendining et al., 2001; Thomsen et al., 1997; Jayasundara et al., 2010; Macdonald et al., 1989). Reported shares of N leaching from animal manure or mineral fertiliser during two to three years after fertiliser addition range between 3% and 10% of applied N, but they also depend on soil type and climatic conditions. Using suction cups, Jayasundara et al. (2010) found that under a maize-maize rotation on silt loam, 4.5–6.9 kg of ^{15}N labelled swine manure N were leached over two years, which is in the same range as the values we found. On sandy soil they found higher values, ranging from 12.8 to 21.5 kg manure N ha^{-1}, equivalent to a relative Ndff of up to 25% of leached nitrate originating from swine manure. It must be noted, though, that total amounts of mineral N leaching found by Jayasundara et al. (2010) were considerably lower than in our experiment (annual mineral N leaching losses were less than 65 kg N ha^{-1} in the first and less than 30 kg N ha^{-1} in the second year after addition of 150 kg N ha^{-1}). These differences might relate to the measurement method: In our study, we used SIAs for measuring nitrate leaching, and as shown by Wey et al. (2022), this method usually yields higher values than suction cups, as the latter cannot fully account for preferential flow through macropores.

Especially within the first measurement period underneath maize between April and September 2018, between 2.3% and 12.1% of leached nitrate derived from fertilisers (**SI B** Fig. 3). Overall, leaching amounts in this rather dry period with high evapotranspiration and low precipitation were small. We assume that the leached nitrate originated from preferential flow through desiccation cracks in the soil, which likely was fostered by several thunderstorms during summer 2018.

We observed the highest nitrate leaching under winter wheat (Fig. 5). Termination of grass-clover ley within a crop rotation is considered a "hot moment" in N cycling and associated with increased losses from nitrate leaching and N_2O emissions due to exacerbated mineralisation of accumulated soil N (Buchen et al., 2017; Velthof et al., 2010; Wagner-Riddle et al., 2020). In the *Gäu* region, but also in other areas with temperate climate, farmers are therefore usually advised to avoid grass-clover termination in autumn (Velthof et al., 2010). However, our results indicated that termination of grass-clover leys in spring followed by maize and a winter cereal just shifts the leaching to the next winter, which was also found by Wey et al. (2022) for fields in the same study region and during the same period. In our study, maize was drilled by rotary band seeding after killing the grass-clover with a broadband herbicide. After maize, fields were ploughed, which might have enhanced mineralisation. However, Helfrich et al. (2020) also observed elevated soil Nmin levels that persisted even two years after ley termination, independent whether ley termination was done by ploughing or purely chemically without any soil tillage. Shifting ley termination from autumn to spring, thus, is not sufficient to prevent nitrate leaching, and further measures might be necessary. These measures might include undersown cover crops for the next winter (Sørensen, 2004; Eriksen et al., 2004; Wachendorf et al., 2006, De Notaris et al., 2018), changes in the crop rotation (e.g. replacing winter wheat by winter barley due to its higher N uptake in fall), or including plants with biological nitrification inhibition capacity into the grass-clover mixture (Coskun et al., 2017).

4.4. Low residual fertiliser value of both cattle slurry and mineral fertiliser

We expected that with greater recoveries of slurry N in soil, also the residual fertiliser NUE would be larger for Slu than for Min. Following on from the discussion in Smith and Chalk (2018), we compared different calculation approaches for assessing the residual recovery of labelled fertiliser N. Calculating N recoveries relative to initially applied amounts neglects N already taken up by the pre-crop or lost in the first year. Therefore, residual recovery should rather be expressed relative to the amount of ^{15}N labelled fertiliser left in soil after harvest of the pre-crop(s) (Smith and Chalk, 2018). However, deriving the residual recovery from measured ^{15}N recoveries in soil after biomass harvest (*residual recovery*$_{soil}$) can be biased by the difficulty of accurately assessing them, due to the dependency on an accurate determination of soil mass, which in turn depends on bulk density. The observed large variation in total N stocks indicates limited accuracy (**SI B** Fig. 4). Furthermore, ^{15}N gets diluted in a large soil N pool, and reliable results can only be obtained when the ^{15}N enrichment clearly exceeds natural abundance. In our study, ^{15}N abundances in topsoil still was 0.38–0.49 atom% at the final sampling which is at least four times natural abundance level in delta notation. In addition, estimates of *residual recovery*$_{soil}$ are blurred by the proportion of ^{15}N in roots and stubble, which might get re-mineralised later. Therefore, we tested an additional approach of accounting for plant N uptake and all measured losses of ^{15}N labelled fertilisers when calculating the residual recovery (*residual recovery*$_{output}$).

Relative to the originally applied amount of N, residual recoveries in plant biomass were greater for Slu than for Min (see 3.1), which agrees with our hypothesis. However, we detected no differences between Min and Slu in *residual recovery*$_{soil}$ (Eq. 5) nor *residual recovery*$_{output}$ (Eq. 6) (Table 4). Both estimates were in a similar range, but values tended to be slightly higher and more variable for *residual recovery*$_{soil}$. In our set-up, where roots and stubble could not be sampled during the ongoing experiment, *residual recovery*$_{soil}$ was probably slightly overestimated, as it did not consider fertiliser N remaining in these plant parts. The greater variability in *residual recovery*$_{soil}$ is also linked to the high uncertainty of total N stocks in the soil (**SI B** Fig. 4). This uncertainty also affected calculations of the cumulated residual recovery in nitrate leaching, plant uptake and soil in succeeding years, which tended to reach values $> 100\%$ (**SI B** Fig. 5).

The low recoveries of residual fertiliser N in succeeding crops are in good agreement with previous studies (e.g. Sørensen, 2004, Glendining et al., 2001, Jensen et al., 1999). The generally low residual recoveries indicate that the availability of residual fertiliser N in soil was low. This goes along with the finding that most residual fertiliser N for both Min and Slu was recovered in the non-microbial organic soil N pool already in the following spring after application (Frick et al., 2022).

This experiment has been conducted on soils with rather high N levels, due to long-term N input and their alluvial origin. High soil N levels combined with a high mineralisation rate likely contribute to both high nitrate leaching and low residual fertiliser N recoveries (Edmeades, 2003). On the other hand, there is evidence that SOM levels are not a major influencing factor on the residual value of fertilisers (Berntsen et al., 2007; Langmeier et al., 2002; Glendining et al., 2001). Rather, mineralisation rate of the remaining fertiliser N might be decisive, which in turn is closely coupled to C cycling (compare 4.2). Sørensen (2004) found that 17–35% of applied slurry ^{15}N-NH_4 was immobilised due to organic matter addition with slurry and not re-mineralised within the following two to three years. Webb et al. (2013) indicated that mineralisation of residual N from animal manure might continue over decades, but gradually loses its agronomic relevance over the course of ten years. In contrast to our results, Sørensen (2004) found lower release rates for residual slurry N than mineral fertiliser N and attributed it to the ongoing immobilising effect of organic material added with the slurry. Sørensen and Amato (2002) reported release rates of organic N to be dependent on soil texture, with less mineralisation of organic N from fertiliser in clayey soils. With both our fields having clay contents of about 22% in the top soil, this could explain the lack of differences between Min and Slu, as mineralisation might have been lowered by the high clay content.

4.5. ^{15}N soil-system balance for mineral fertiliser and cattle slurry

We measured crop N uptake and all major loss pathways from both ^{15}N labelled cattle slurry and ^{15}N labelled mineral fertiliser in the field. Slightly larger and more variable cumulative recoveries (Fig. 3) for Slu than for Min are in accordance with others (Sørensen, 2004) and hint to less accurate estimates for Slu due to less homogenous distribution in soil (Bosshard et al., 2009). All measured pools within this study summed up to 85–94% of applied ^{15}N and complemented with NH_3 emission added up to approximately 100%, giving a good indication that we obtained reliable data (Fig. 3). The remainder could be attributed to dissolved organic N (DON) leaching or N_2, NO or N_2O emission. Based on assumptions derived from Van Kessel et al. (2009), DON leaching in our study might account for 1–2.5% of applied fertiliser N (compare **4.3**). Emissions of N_2O are usually estimated to account for less than 1% of applied N (IPCC, 2006). However, losses as N_2 can be considerably higher than as N_2O, as also indicated by Oenema et al. (2007) who found that up to 7% of excreted N could get lost via denitrification when all losses via denitrification, including N_2 losses, are taken into account. Furthermore, upon grass-clover termination usually elevated N_2O emission from mineralisation of incorporated stubbles and roots can be expected (Krauss et al., 2017). Since ^{15}N recovery in crops and presumably also in stubble and roots was higher in Min than in Slu in the first year, this could hint to higher N_2O losses from Min than from Slu upon grass-clover termination. This loss pathway could explain the slightly lower overall recovery for Min than for Slu, especially at Field B.

5. Conclusion

Following the fate of ^{15}N labelled cattle slurry and mineral fertiliser throughout three cropping seasons, we found only minor shares (< 8%) of the added slurry or mineral fertiliser N leached. However, significantly more slurry than mineral fertiliser N was leached. Overall, the major share of nitrate leaching originated from the mineralisation of soil N, which in turn contained accumulated N from earlier manure applications and of N built-up during the grass-clover phase. Since we found the highest leaching after the termination of grass-clover, it appears critical to specifically control the build-up of soil organic N stocks under grass-clover and take prolonged mineralisation upon its termination into account. Further studies should focus on the response of soil N dynamics to reduced N inputs combined with the role of C inputs, crop rotations and soil tillage, in order to reduce leaching losses while avoiding SOM depletion.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Author contributions

HF, AO, EF and EB designed the experiment. HF conducted the field experiment, performed lab work, and wrote the manuscript. Internal revisions were supported by AO, EF, and EB. All co-authors have commented on a draft of the manuscript and approved the final version.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.agee.2022.108093.

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