



Article

Effects of Adapted N-Fertilisation Strategies on Nitrate Leaching and Yield Performance of Arable Crops in North-Western Germany

Insa Kühling 1,* D, Mareike Beiküfner 2, Maria Vergara 2 and Dieter Trautz 2

- Faculty of Agricultural and Nutritional Sciences, Agronomy & Crop Science, Kiel University, Hermann-Rodewald-Str. 9, 24118 Kiel, Germany
- ² Faculty of Agricultural Sciences and Landscape Architecture, Sustainable Agro-Ecosystems, Osnabrück University of Applied Sciences, Am Krümpel 31, 49090 Osnabrück, Germany; m.beikuefner@hs-osnabrueck.de (M.B.); m.vergara-hernandez@hs-osnabrueck.de (M.V.); d.trautz@hs-osnabrueck.de (D.T.)
- * Correspondence: kuehling@pflanzenbau.uni-kiel.de

Abstract: Groundwater pollution with nitrate is a big challenge for drinking water abstraction in regions with intensive agricultural land-use, specifically with high livestock densities on sandy soils in humid climates. Karst aquifers with high water flow velocities are extremely vulnerable to this problem. To cope with this situation, a field trial with an installation of ceramic suction cups under a randomised block design with a typical north-German cropping sequence of silage maize-winter wheat-winter barley was established in a karst water protection zone. Over three years, reduced nitrogen (N) application rates and N type (mineral or combined organic + mineral fertilisation) were tested for their effects on crop yields and leachate water quality below the root zone. Results showed no significant reductions in crop yields with 10/20% reduced N rates for cereals/maize and only slight reductions in cereal protein content. Nitrate concentration from adapted N rates was significantly lower in treatments with an application of organic fertilisers $(-7.74 \text{ mg NO}_3\text{-N I}^{-1})$ with greatest potential after cultivation of maize; in only mineral fertilised plots the effect was smaller (-3.80 mg NO₃-N l⁻¹). Cumulative leaching losses were positively correlated with post-harvest soil mineral nitrogen content but even in unfertilised control plots losses >50 kg N ha⁻¹ were observed in some crop-years. Reduced N rates led to decreased leaching losses of 14% (6.3 kg N ha⁻¹ a⁻¹) with mineral and 29% (20.1 kg N $ha^{-1}a^{-1}$) with organic + mineral fertilisation on average overall cops and years. The presented study revealed the general potential of adapted fertilisation strategies with moderately reduced N applications (-10/-20%) to increase leachate water quality without affecting significantly crop yields. However, regionally typical after-effects from yearlong high N surpluses in livestock intensive farming systems are a limiting factor.

Keywords: NO₃; drinking water protection; nitrogen losses; karst aquifer; fertiliser ordinance; suction cups; nitrogen surplus; N balance



Citation: Kühling, I.; Beiküfner, M.; Vergara, M.; Trautz, D. Effects of Adapted N-Fertilisation Strategies on Nitrate Leaching and Yield Performance of Arable Crops in North-Western Germany. *Agronomy* **2021**, *11*, 64. https://doi.org/ 10.3390/agronomy11010064

Received: 1 December 2020 Accepted: 28 December 2020 Published: 30 December 2020

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/).

1. Introduction

Nitrogen (N) plays an important role in global agriculture: on the one hand, more than 50% of the world's population is nourished by N-fertilised crops [1]; on the other hand, the environmental impacts of N use is far beyond planetary boundaries [2,3], mainly caused by agriculture [4,5]. For feeding the growing global population, concepts, such as sustainable intensification, requests balanced production systems between optimised yields and environmental impacts [6–9].

In intensive production systems with high livestock densities as typical for northwestern Germany [10], high N balance surpluses are likely to cause nitrate (NO_3) contamination of groundwater bodies, and applications of organic N sources additionally boost the

Agronomy **2021**, 11, 64 2 of 16

problem [11]. NO_3 leaching from high N surplus occurs, especially in regions with high amounts of precipitation on sandy soils with low retention potential [12,13], and causes the main damage of water bodies [14]. In drinking water abstraction areas, this is, furthermore, related to high external costs, since high NO_3 concentrations are known to be harmful for human health [5,11]. Besides social costs for drinking water purification, further environmental impacts are caused by NO_3 losses, such as indirect greenhouse gas (GHG) emissions [15] and degradation of other ecosystem services [16]. Some authors argue that such environmental off-site damages have to be calculated per unit yield e.g., [17,18], but in terms of groundwater protection, area scaled estimations are preferable over yield scaled estimation [19].

The European and national legal frameworks have favoured the Good Agricultural Practices (GAP) and cover, with several laws and regulations, the protection and monitoring of good quality of water bodies [20,21]. Across the European Union, regional adapted policies, according to differences in N balance surplus, are possible [22]. In Germany, this was implemented by the Fertiliser Ordinance (FO) with regulations for yield scaled upper limits for N fertilisation [23]. To ensure efficient plant nutrition, specifically in humid climates, some N balance surpluses are unavoidable [13], for example the sustainability evaluation tool REPRO rates 0 to $50\,\mathrm{kg}\,\mathrm{ha}^{-1}\,\mathrm{a}^{-1}$ as fully sustainable [24]. Nevertheless, there is a broad consensus about the necessity of demand-oriented N fertilisation to avoid leaching losses that increase with the amount of N applied with excessive growth beyond the agronomic optimum [25–30].

Well-known strategies to reduce nitrate leaching, besides a reduction of N inputs, or rather a better synchronisation of N inputs and crop demands to achieve lower surpluses, are, for example, cultivation of catch crops [31–34]. In typical German cropping sequences, this is possible before spring-sown crops. Chemical solutions, such as fertilisers with nitrification inhibitors, can help to bridge leaching risks between application and plant uptake [34,35]. Moreover, organic farming is promoted as a measure to mitigate groundwater pollution due to area-based livestock densities and waiving of mineral N fertilisers [36,37]. Lower NO₃ leaching risks were observed for organic farming systems in European studies [37–39]. N supply in organic farming systems is often based on biological N fixation by legume crops [40,41] with additional benefits, such as promoting biodiversity from integrating in crop rotations [42,43].

Usually, N leaching losses from agricultural fields are either measured with suction cups or plates directly below the root zone, directly calculated/modelled from measured soil mineral nitrogen concentrations in typical depths (e.g., 0–90 cm), or indirectly calculated from estimates (e.g., N balance surplus). Denitrification processes between the root zone and the groundwater surface are seldom part of field investigations and little knowledge about the magnitude of denitrification exists [44]. However, some geological undergrounds request special attention for minimised leaching losses directly below the root zone, since percolation time and denitrification potential are geogenic limited. Karst aquifers, for example, have special and complex characteristics and differ significantly from other aquifers with a high heterogeneity, large voids, and rapid flow velocities [45].

Against this background, a pilot and demonstration project was launched within an intensively farmed water protection area of a karst aquifer with nitrate concentration above the European Union (EU) drinking water limit of $50\,\mathrm{mg}\,\mathrm{l}^{-1}\,\mathrm{NO}_3$ (= $11.3\,\mathrm{mg}\,\mathrm{l}^{-1}\,\mathrm{NO}_3$ -N). The objectives of this study were to investigate the effects of adapted fertilisation strategies in terms of N rate and N type (mineral or organic) on yield performance and leachate water quality in a typical cropping sequence with winter wheat, winter barley, and silage maize.

2. Materials and Methods

2.1. Study Site

The study site is located within the drinking water abstraction area Belm-Nettetal at 52.3° N, 8.1° E in north-western Germany. The climate is temperate oceanic (Cfb [46]) with mean annual air temperature of 9.5° C and mean annual precipitation sum of $883 \, \text{mm}$ [47].

Agronomy **2021**, 11, 64 3 of 16

Agricultural land use is dominant (58%) and mostly at high input intensity with high livestock densities (1.5–3 livestock units per ha) as typical for this region. The site is characterised by a karst aquifer with loamy sand leading to a high leaching potential [45]. The hydraulic conductivity is $26\,\mathrm{cm}\,\mathrm{d}^{-1}$ and between 17 and $46\,\mathrm{cm}\,\mathrm{d}^{-1}$ in the topsoil and subsoil, respectively. The soil type is classified after WRB, as Plaggic Anthrosol [48], with 1.16% organic carbon in the top layer, pH values between 5.7 and 6.2, and 52/42/6% of sand/silt/clay. The initial soil conditions comprised a phosphorus content of $86.7\,\mathrm{mg}\,\mathrm{kg}^{-1}$, a potassium content of $70.0\,\mathrm{mg}\,\mathrm{kg}^{-1}$ and a C:N ratio of 7.93. Before installation of the trial, the field was commonly managed by a conventional fattening farm with a cereal/maize dominated crop rotation.

2.2. Experimental Setup and Agronomic Management

For investigating the effects of different nitrogen fertilizer types and application rates on leachate water quality a complex field trial with the cropping sequence silage maize winter wheat—winter barley was established. During three consecutive seasons, each crop was grown in each year in a randomised block design, starting with winter cereals and catch crop sowing in autumn 2016. Within each crop, six different N-fertiliser treatments were applied with three replications. These six N-fertiliser treatments differed between fertiliser type and application rate. The application rates were 0 kg N ha^{-1} , 50 kg N ha^{-1} (applied as mineral fertiliser) or based on the fertiliser ordinance (FO) N-need estimation as well as reduced N-application according to the FO by -10% for cereals, and -20% for maize (FO red). These two different application rates were applied either as mineral fertiliser (m) or as combination of organic and mineral fertiliser (o) which led to the following treatments: 0, 50, FO_m, FO_o, FO_m red and FO_o red. The FO as the German legal framework for GAP calculates crop specific N-needs under consideration of yield expectations, previous crop effects, catch crop effects and previous organic fertiliser application rates; therefore, the individual rates changed between the years [23]. For calculating the total amount of N-application in the FO treatments, plant available soil mineral nitrogen (SMN) at the beginning of the vegetation period (February for cereals, April for maize) was subtracted from crop specific N-need. The total amount of N applied (Table 1) was split into two or three applications (Table 2), whereby the third dose was skipped under reduced and 0/50 treatments. On average, SMN in spring was $24(\pm 9.6)/30(\pm 13.6)/44(\pm 6.2)$ kg ha⁻¹ for barley, wheat, and maize, respectively.

Table 1. Applied N-fertiliser rates for the fertiliser ordinance (FO) treatments within crop and year. (0 and 50 kg N ha^{-1} treatments were constant in all years).

	N-Fe	ertiliser Applied (kg N h	na ⁻¹)
	2016/2017	2017/2018	2018/2019
Barley			
FO_m	134	174	153
FOo red.	119	156	140
FO _o	134	163	141
FOo red.	119	145	125
Maize			
FO_m	143	164	153
FOo red.	114	124	121
FO_{o}	143	149	132
FOo red.	114	123	108
Wheat			
FO_m	141	203	186
FOo red.	125	181	169
FO_0	141	189	174
FOo red.	125	170	158

Agronomy **2021**, 11, 64 4 of 16

2016/2017			2017/2018			2018/2019			
Date	Barley	Maize	Wheat	Barley	Maize	Wheat	Barley	Maize	Wheat
Sowing	14.10.	26.04.	14.10.	15.10.	23.04.	07.11.	05.10.	30.04.	09.10.
Seeds m^{-2}	320	9	300	275	9	380	275	9	350
Cultivar	Tamina	ES Metronom	Anapolis	Wootan	Baydinter	Benchmark	Wootan	Baydinter	Benchmark
	15.03.*	19.04.*	15.03.*	13.02.*	19.04.*	13.02.*	13.03.*	24.04.*	13.03*
N application	19.04.*	26.04.	19.04.*	05.03.	23.04.	05.03.	20.03.	30.04.	20.03.
	22.05.	26.05.*	22.05.	03.05.	03.05.	03.05.	17.04.	08.05.	17.04.
Harvest	19.07.	18.10.	28.07.	05.07.	11.09.	18.07.	09.07.	09.09.	30.07.

Table 2. Description of sowing, N-fertilisation and harvest for each crop and year.

Primary tillage was done with a chisel cultivator; seedbed preparation took place with a rotary cultivator. Plot size was 30 m² and row spacing between was 12.5 cm for cereals and 75 cm for maize. After harvest, cereal straw was removed, and plant residues (stubbles, roots) were incorporated. A catch crop of phacelia and buckwheat was grown after barley harvest for continuous soil coverage during the winter period before maize. Plant protection and fertilisation of basic nutrients (P, K, Ca) was performed as common upon demand within each crop. Cultivar selection and timings were done as typical for the water protection zone in each year. Organic N-fertilisation in the FO₀ treatments took place with pig slurry after analysing NO₃ and NH₄ content each year for calculating application rates. The slurry was applied on the surface with drag hoses and incorporated before planting of maize. For mineral N-fertilisation, we used ammonium sulphate nitrate and calcium ammonium nitrate. Detailed descriptions of the agronomic management operations for each crop and year are given in Table 2.

2.3. Field Measurements and Post-Harvest Analyses

For quantifying soil mineral N (SMN), soil samples were taken at depths of 0–30 cm, 30–60 cm, and 60–90 cm at the beginning of the vegetation period, after harvest, and at the end of the vegetation period in each year. Soil samples were collected in each plot (three replicates per plot) and unified per fertiliser treatment and crop to a mixed sample. SMN status was determined by analysing nitrate and ammonium up to 90 cm depth [49]. For grain yield determination of barley and wheat, the plots were threshed with a plot combine harvester. Silage maize was harvested manually as whole plants at two different spots per plot, with a size of 9 m² total, and chopped afterward. Protein content of grain (barley, wheat) and silage maize samples was determined by using near-infrared spectroscopy.

2.4. Nitrate Leaching

For investigating nitrate concentrations in the leaching water, one ceramic suction cup per plot was installed in 80 cm soil depth below the undisturbed root zone at an angle of 26°. A vacuum of $-200\,\text{hPa}$ was applied continuously to the suction cups to gather percolating water during the winter season (October–March) in each experimental season, starting after the first harvest in autumn 2017 and allocating the leachate to the previous crop. The collected leachates were analysed biweekly as mixed samples of the three replicates per fertiliser treatment and crop. Nitrate concentration was determined according to VDLUFA [50] and measured with a spectrophotometer (Perkin Elmer Lambda 25, Waltham, MA, USA).

Leaching losses were calculated from measured concentrations and simulated leachate water from a 3-layer water balance model [51]. The model was evaluated with continuously logged soil moistures in 40 cm and showed a good performance ($R^2 = 0.91$, Nash–Sutcliffe–Efficiency = 0.67). A detailed description of the used input data and parametrisation of the model can be found in Trautz et al. [52].

^{*} organic fertiliser was applied in FOO treatments.

Agronomy **2021**, 11, 64 5 of 16

2.5. Data Analyses

For statistical analyses, we used R [53] to conduct an analysis of variance followed by Tukey HSD-test for the yield data with the package "agricolae" [54]. Nitrate concentrations were analysed by effect sizes following the bootstrap estimation statistics with the R package "dabestr" [55,56].

3. Results

The experimental seasons showed different climate conditions, but received all below average precipitation (75, 65, 69% for 2016/2017, 2017/2018, and 2018/2019 compared to the long-term average) with above average air temperatures (+0.4, +1.5, +1.5 $^{\circ}$ C) (Figure 1). Only the leachate period after the last harvest was warmer and wetter (+11% precipitation). Specifically, dry and warm spring and early summer months affected crop yields compared to typical seasons.

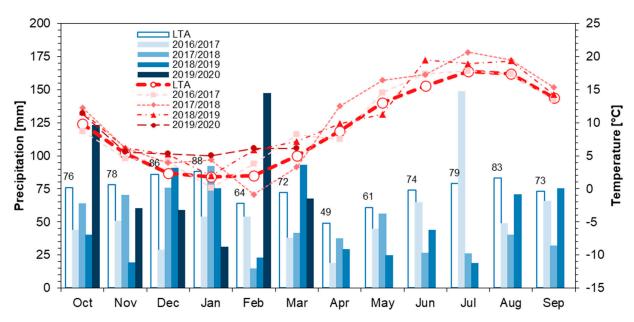


Figure 1. Monthly precipitation sums and mean air temperatures for the observed growing seasons and long-term average values (LTA) Data source: [47].

3.1. Yield and Yield Quality

Observed yields showed a clear response to fertiliser level with lowest in unfertilized control plots and on average highest in FO_m plots (Table 3). In comparison of the recommended (FO) against the reduced (FO red.) treatments, relative yields of reduced plots were between 87 and 110% of the FO and between 89 and 114% with mineral and organic + mineral fertilisation, respectively. On average, the reduced application rates led to slightly lower yields for cereals (93% wheat, 99% barley) and slightly higher yields in silage maize (104%), none of the comparisons were significant. The differences between the FO and 0/50 treatments increased over time. The N response of silage maize yield was less pronounced than those of cereals (Figure 2). In terms of grain quality, the reduced treatments showed slightly lower protein concentrations with up to 5% and 3% relative losses for wheat and barley, respectively. The differences increased over time, but were only significant for two comparisons (barley in 2018 with FO_m and wheat in 2019 with FO_o fertilisation).

Agronomy **2021**, 11, 64 6 of 16

Table 3. Yield (grain yield at 86% dry matter (DM) for cereals and total DM yield for silage maize) and protein concentrations (\pm standard error) with results of Tukey-test within mineral (m) and organic + mineral (o) fertiliser treatments (HSD_{0.05}); FO: fertiliser ordinance, red: reduced; * significant.

		Winter Barley		Silage	Maize	Winter Wheat		
		Yield (dt ha ⁻¹)	Protein (% DM)	Yield (dt ha^{-1})	Protein (% DM)	Yield (dt ha^{-1})	Protein (% DM)	
Year	Treatment							
2017	$\begin{array}{c} 0\\ 50\\ FO_m\\ FO_m \ red.\\ HSD_{0.05\ min}\\ FO_o \end{array}$	27.61 (± 1.15) 46.64 (± 0.56) 56.34 (± 1.14) 53.15 (± 1.71) 5.50 53.76 (± 1.97)	11.33 (± 1.09) 12.37 (± 1.09) 11.17 (± 1.17) 11.37 (± 1.11) 5.05 9.80 (± 0.12)	177.98 (± 8.63) 216.84 (± 1.09) 220.92 (± 3.12) 225.48 (± 11.89) 34.11 197.56 (± 9.88)	$5.37 (\pm 0.17)$ $5.60 (\pm 0.15)$ $6.33 (\pm 0.09)$ $6.80 (\pm 0.10)$ 0.59 $5.97 (\pm 0.20)$	21.89 (± 2.29) 39.46 (± 1.03) 56.93 (± 4.17) 52.93 (± 1.32) 11.44 48.67 (± 3.75)	14.23 (± 2.02) 11.70 (± 0.85) 11.43 (± 0.84) 10.77 (± 0.09) 5.32 12.03 (± 0.89)	
	FO _o red. HSD _{0.05 org}	49.88 (\pm 2.62) 9.15	11.17 (± 1.13) 3.14	224.78 (\pm 15.14) 50.16	6.23 (± 0.58) 1.72	$46.07 (\pm 4.24)$ 15.70	12.00 (± 1.02) 3.74	
2018	0 50 FO_{m} FO_{m} red. $HSD_{0.05 \ min}$	$\begin{array}{ccc} 25.45 & (\pm~0.84) \\ 46.80 & (\pm~1.46) \\ 64.09 & (\pm~0.65) \\ 65.25 & (\pm~0.74) \\ 4.43 & \end{array}$	$9.93 (\pm 0.07)$ $9.40 (\pm 0.15)$ $14.47 (\pm 0.13)$ $13.87 (\pm 0.09)$ 0.52	128.16 (± 3.96) 176.77 (± 3.41) 160.94 (± 9.36) 177.00 (± 5.47) 27.22	$3.13 (\pm 0.09)$ $3.53 (\pm 0.49)$ $3.80 (\pm 0.40)$ $3.60 (\pm 0.35)$ $1.65 (\pm 0.09)$	29.63 (± 2.01) 54.54 (± 1.78) 85.85 (± 1.35) 86.05 (± 1.27) 7.40	$\begin{array}{ccc} 9.13 & (\pm 0.23) \\ 8.57 & (\pm 0.12) \\ 13.50 & (\pm 0.27) \\ 13.00 & (\pm 0.06) \\ 0.85 & \end{array}$	
	FO _o FO _o red. HSD _{0.05 org}	57.55 (± 1.69) 57.62 (± 0.58) 4.92	11.97 (± 0.42) 11.27 (± 0.18) 1.27	$148.88 \ (\pm 10.41)$ $154.47 \ (\pm 10.07)$ 40.24	$3.83 (\pm 0.52)$ $3.57 (\pm 0.12)$ 1.48	$80.20 (\pm 1.25)$ $74.53 (\pm 2.72)$ 8.31	11.07 (± 0.23) 10.37 (± 0.23) 0.92	
2019	0 50 FO _m FO _m red. HSD _{0.05 min} FO _o FO _o red. HSD _{0.05 org}	$\begin{array}{cccc} 15.63 & (\pm 1.33) \\ 28.20 & (\pm 5.33) \\ 51.33 & (\pm 5.78) \\ 55.50 & (\pm 3.19) \\ 19.50 & & & \\ 43.13 & (\pm 6.13) \\ 41.01 & (\pm 2.59) \\ 18.43 & & & \end{array}$	$\begin{array}{cccc} 8.17 & (\pm~0.47) \\ 6.80 & (\pm~0.10) \\ 9.73 & (\pm~0.09) \\ 8.97 & (\pm~0.35) \\ 1.36 & & \\ 7.97 & (\pm~0.13) \\ 7.67 & (\pm~0.22) \\ 0.71 & & \end{array}$	123.17 (\pm 4.33) 151.38 (\pm 16.60) 143.75 (\pm 4.95) 139.71 (\pm 7.07) 43.48 153.40 (\pm 4.52) 141.93 (\pm 4.86) 18.39	$\begin{array}{cccc} 2.17 & (\pm~0.07) \\ 2.70 & (\pm~0.27) \\ 2.67 & (\pm~0.14) \\ 2.47 & (\pm~0.17) \\ 0.80 & & \\ 2.53 & (\pm~0.03) \\ 2.70 & (\pm~0.06) \\ 0.19 & & \end{array}$	22.93 (± 2.87) 46.87 (± 8.17) 113.87 (± 3.71) 98.83 (± 7.06) 26.61 83.28 (± 4.00) 73.82 (± 13.19) 38.34	$\begin{array}{cccc} 8.00 & (\pm~0.21) \\ 7.37 & (\pm~0.14) \\ 11.43 & (\pm~0.23) \\ 10.83 & (\pm~0.27) \\ 1.00 & \\ 9.67 & (\pm~0.12) \\ 8.93 & (\pm~0.12) \\ 0.47 & \\ \end{array}$	

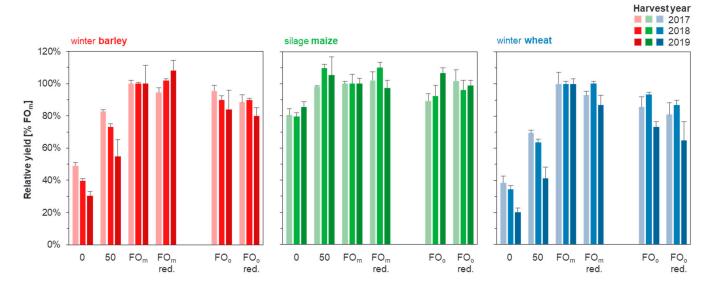


Figure 2. Mean relative yield compared to FO_m treatment (grain yield at 86% dry matter for cereals and total biomass dry matter yield for silage maize) (N = 3, error bars indicating 1 standard error of the mean).

Agronomy **2021**, 11, 64 7 of 16

3.2. Nitrate Concentrations

Nitrate concentrations below the root zone showed a typical dilution pattern during the leachate period, with high initial values in the beginning and decreasing concentrations towards the end of the winter for all crops. On average, fertilizer treatments with organic sources led to higher nitrate concentrations (+ $1.9\,\mathrm{mg\,NO_3\text{-}N\,l^{-1}}$) as well as to a higher potential for decreasing concentrations by reduced fertilisation (Figure 3). In average of all years, the highest concentrations were found after the harvest of wheat, followed by maize and barley. In comparison of the years, nitrate concentrations showed a clear pattern according to the total drainage with the highest mean concentrations of $35.9\,\mathrm{mg\,NO_3\text{-}N\,l^{-1}}$ in 2018 ($159\,\mathrm{mm}$), followed by $20.3\,\mathrm{mg\,NO_3\text{-}N\,l^{-1}}$ in 2017 ($159\,\mathrm{mm}$), and $14.1\,\mathrm{mg\,NO_3\text{-}N\,l^{-1}}$ in 2019 ($305\,\mathrm{mm}$), which were all above the legal limit for drinking water of $11.3\,\mathrm{mg\,NO_3\text{-}N\,l^{-1}}$.

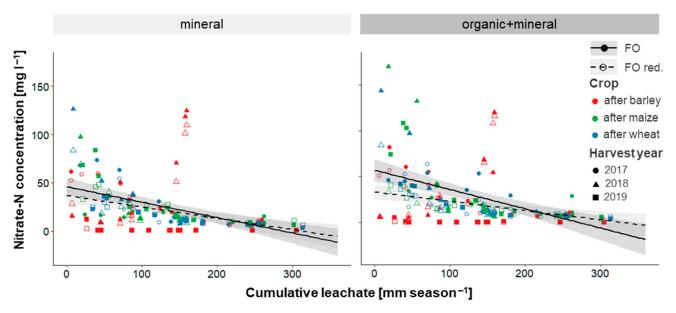


Figure 3. Nitrate-N concentrations over time during the leachate periods for fertilisation after Fertiliser Ordinance (FO) and reduced by 10/20% (FO red.).

Figure 4 shows that even without fertiliser application, or with only moderate N-rates $(50 \,\mathrm{kg \, ha^{-1}})$, similar nitrate concentrations below the root zone were observed in all crops. In direct comparison of recommended and reduced N-application rates, negative effect sizes revealed the potential for general reduction of nitrate concentrations in leachate (Figure 3). Specifically, in maize with combined organic and mineral N-sources (FO₀) this effect was clearly observed and led to significant lower NO₃-N concentrations of 50% (32.5 to 16.1 $\mathrm{mg \, l^{-1}}$). On average, among all crops, the FO₀ treatments showed a slightly lower, but still significant reduction potential of 28% by reduced application rates (Table 4).

Agronomy 2021, 11, 64 8 of 16

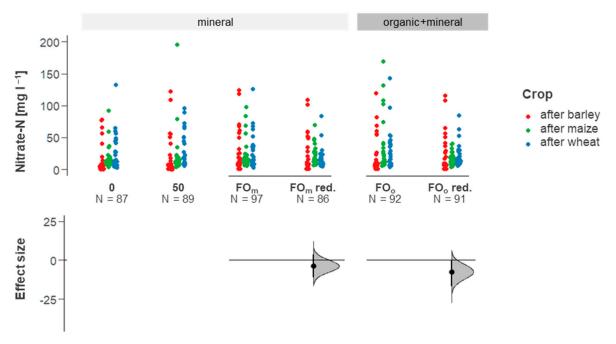


Figure 4. Estimation plot and effect sizes for NO₃-N concentrations under different fertiliser treatments and direct comparisons between fertiliser ordinance recommended (FO) vs. reduced (FO red.) fertilisation by fertiliser type (m: only mineral, o: combined organic + mineral) for all experimental seasons (N: sample size).

Table 4. Effect size (ES, mean difference) with 95% confidence intervals of reduced vs. recommended N-fertilisation for only mineral and combined organic and mineral applications for all crops over three years (N: sample size reduced/normal fertilisation; *: significant difference).

	Nitrate-N-Concentration (mg ${ m l}^{-1}$)							
		Only Mineral			Organic + Mineral			
	ES	95% CI	N	ES	95% CI	N		
Barley	-3.42	[-18.20; 11.20]	33/33	2.32	[-12.60; 17.50]	30/31		
Maize	-1.12	[-12.20; 7.78]	25/31	-16.10*	[-34.60; -3.93]	31/31		
Wheat	-6.69	[-18.50; 3.05]	28/33	-9.44	[-24.00; 1.17]	30/30		
All	-3.80	[-11.20; 3.50]	86/97	<i>−7.74</i> *	[-17.00; -0.16]	91/92		

3.3. Nitrate Leaching Losses

Calculated leaching losses from nitrogen concentrations and modelled leaching water are presented in Figure 5. Even though crops and seasons were different, a general pattern of lower leaching losses from less fertiliser application was visible. In direct comparisons of the recommended vs. reduced FO treatments, cumulative leaching losses were always lower with reduced fertilisation. However, leaching losses from unfertilised and moderately fertilised (50 kg ha⁻¹) plots were much more heterogeneous between crops and years.

Agronomy **2021**, 11, 64 9 of 16

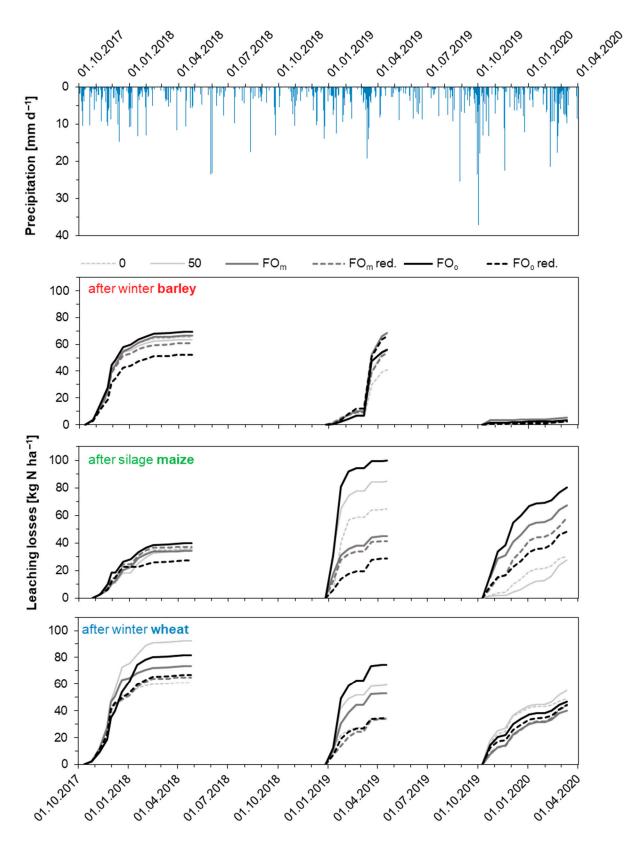


Figure 5. Cumulative leaching losses over time for all fertiliser treatments (FO: fertiliser ordinance, red: reduced, m: only mineral, o: organic + mineral).

The correlation between post-harvest SMN and cumulative leaching losses was significant positive (Figure 6) and showed that even with negative N balances (see Supplementary Materials) serious amounts of nitrogen remained on the field in autumn. The maximum N

Agronomy 2021, 11, 64 10 of 16

balance surplus to reach a below threshold nitrate concentration of $<50\,\mathrm{mg}\,l^{-1}$ would be $37\,\mathrm{kg}\,N\,ha^{-1}$ under long-term average conditions (325 mm leachate water). Since all experimental seasons were dryer, the theoretical limits of allowed N surplus were even lower with 29, 18 and 35 kg N ha⁻¹ for the consecutive harvest years. Except for wheat in 2019, all treatments in all crops and years failed this limit and thus resulted in high losses. Under a much better developed catch crop, compared to the previous years, significantly lower concentrations and cumulative leaching losses occurred after barley in the last leachate season.

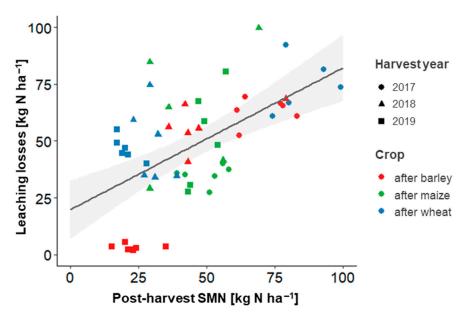


Figure 6. Relation between post-harvest soil mineral nitrogen (SMN) and nitrogen leaching losses below the root zone.

4. Discussion

4.1. Yield Effects

In general, yields from the observed above average warm and dry experimental seasons were lower than from normal years. Especially after the extreme warm and dry harvest in summer 2018, tillage and sowing of the following winter cereals was challenging and led to poor stand establishments before winter, most pronounced in barley. Hence, yields in 2019 were tendentially the lowest. The main focus was the comparison between standard fertilisation as recommended after FO and the reduced N-level by 10/20% (cereals/maize). After three years, no significant yield effects from reduced N-fertilisation was observed, neither with only mineral nor with combined organic and mineral fertilisation. Other studies reported significant and immediate yield losses, starting already with little reductions of N-fertilisation, specifically for winter cereals [13,57]. The N-response of maize yield was lower compared to the observed cereals, which is a typical difference between winter and spring-sown crops since maize benefits from synchronous N-uptake with mineralisation over summer [58]. Similar effects of high maize yields even without fertilisation were reported by Kayser et al. [59], and might by typical for the land-use history in regions with high livestock densities.

Yields from only mineral nutrition were on average on a higher level and more stable compared to partially organic fertilisation treatments. In our experiment FO_0 treatments received on average 60% N from organic sources in cereals, and 75% in maize, but the tendency of lower yield through flatter N response functions from organic fertilisers as described by, e.g., Sieling [57], were still visible with additional mineral N.

We observed slightly lower grain protein content with an increasing trend over time. Even though, during the duration of this experiment, these differences were without Agronomy **2021**, 11, 64 11 of 16

price effects for wheat so far. In general, this must be considered for future evaluations. However, the effects of reduced N-fertilisation on grain protein concentration were difficult to compare from this experiment since all agronomic management operations took place in close coordination, with practical farmers in the water protection area. Specifically, the split of the N-levels changed over time towards higher rates at earlier fertilisation dates. Together with dry and warm climate conditions, several factors besides adapted total N-levels were likely to contribute to differences in protein content.

4.2. Nitrogen Leaching

4.2.1. N-Level

N leaching losses are closely related to the amount of applied N. Linear models, such as what was proposed by IPCC [15], after Stehfest and Bowman [60], allocated 24% to leaching, the estimation of 19% leaching losses from a meta-analysis by Lin et al. [61] was a bit lower. Wang et al. [29] proposed to use a quadratic fit $(0.0003N^2 + 0.0284N)$ to better reflect differences in low and above optimum rates from a meta-analysis as well. All of these approaches are poorly able to predict the situation from our experiment since they all worked without an intercept, whereas we observed a significant amount of N leaching in unfertilised plots $(46 \text{ kg N ha}^{-1} \text{ intercept from linear regression model})$. A review by Zhou et al. [17] suggested, from 69 wheat experiments worldwide, a linear model with 8.4 kg N ha^{-1} intercept, as well as an exponential model with $16.9 \text{ kg N ha}^{-1}$ that fits much better with our results. On the contrary, their meta-analysis for maize with a negative intercept was even worse for our situation [17]. This emphasises the specific situation of yearlong fertilisation with high amounts of manure in regions with intensive animal husbandry on sandy soils and shows the limitations of global estimations for leaching potential as a fraction of applied N.

Our results showed the general potential to reduce leaching losses, even with very low reductions of applied N by only 10 or 20%, especially if organic fertiliser was applied, but only slight and not significant reductions in yield. In contrast, Goulding [26] reported from the long-term Broadbalk trial at Rothamsted considerable yield reductions below the economic optimal N rate of 144 kg ha⁻¹, and small reductions of N leaching below this point, compared to the steep increase of leaching losses above the economic optimum. Similar results were published from Swedish modelling experiments, with exponentially increased leaching losses above recommended optimal N rates and little effects below, but they only investigated spring cereals after bare fallow [62]. Moreover, Delin and Stenberg [18] described exponentially increasing leaching losses, but only at N rates beyond yield responses of 10 kg grain per kg N fertiliser. On the other hand, some studies revealed similar results to our experiment: Wachendorf et al. [63] described a steep quadratic increase of N leaching losses from maize on sandy soil for N rates between 50 and 150 kg ha⁻¹.

Overall, leaching is not only affected by the amount of N fertiliser, but also from soil mineralisation. Lysimeter experiments with labelled N from New Zealand showed for example only small contribution of applied fertilizer compared to non-labelled leachate and no significant differences between fertilised plots and unfertilised control [64]. Especially on sandy soils that received organic manure this contribution should not be underestimated [13].

4.2.2. N-Type

In most of the observed crop years, cumulative leaching losses from organically fertilised plots were higher than from plots that received only mineral N, which was also described by Di and Cameron [11]. Furthermore, the highest nitrate concentrations at the beginning of the leachate period in early winter were measured under plots with organic fertilisation as well as the largest differences in concentrations and leaching losses between FO recommended and reduced. At the same time, yield responses on reduced N rates were on the same level as with mineral N application. Together this led to the highest potential for both ecological and economic effective water protection by moderately reduced N rates

Agronomy **2021**, 11, 64 12 of 16

in combined organic and mineral fertiliser regimes, specifically for silage maize, where this is a typical production system in north-western Germany. Another study from Lower Saxony also confirms high effects on leaching losses, but only little yield response in silage maize, especially from pig slurry [59].

4.2.3. Catch Crop Effect

Catch crops or cover crops are known to be an effective measure to minimise nitrogen leaching losses [31,32,41], but their mitigation potential is dependent from a successful stand establishment, which underlies a large yearly variability [65]. In the observed cropping sequence, a catch crop was sown after barley before spring crops. Since the crop development was extremely poor in the first two experimental seasons due to extremely dry conditions after harvest of the main crop, N leaching losses after barley were comparable to those after wheat without a catch crop. In the last experimental season, which was the wettest one with good amounts of precipitation after sowing of the catch crop, a good stand development showed huge mitigation potential by significant lower cumulative leaching losses, as well as lowest nitrate concentrations after barley.

4.3. Perspectives

With this study, we investigated the effects of adapted fertilisation strategies on leachate water quality below the root zone as an indicator for groundwater quality in a drinking water abstraction area. We did not investigate the processes during percolation between the root zone and the groundwater table surface, where only little knowledge about the magnitude of denitrification is available [44]. Furthermore, this denitrification potential is mentioned to be limited between 10 and 200 years [66], and may additionally contribute to N₂O losses [59]. This underlines the necessity to reduce N losses already within the root zone, not only in very sensitive karst aquifers for sustainable and groundwater-friendly farming systems in the long run. There are several strategies described to successfully contribute to reduced N surpluses. Besides homogeneously adapted N-levels, the potential of spatial within-field variation through precision farming technologies was demonstrated in Western Australia's wheat belt [67]. Chemical solutions, such as slow release or controlled release fertilisers [35], can enable a better synchronisation of N supply and plant demand [11]. Such effects, as well as adapted application technologies, were less effective for decreasing reactive N based environmental damage compared to lower fertilizer amounts as a simulation from Ontario, Canada [68]. Organic farming is known to have significant lower N surpluses with consequently lower leaching risks, and is already promoted as an agro-environmental scheme in some water protection areas across Germany (e.g., public water suppliers for Munich and Leipzig [69,70]). Based on a systems comparison in northern Germany, Biernat et al. [71] observed significantly lower area scaled nitrate leaching losses under organically managed fields than from conventional farming. Comparatively lower yields are of minor importance in terms of area related water protection and claims for yield scaled estimations e.g., [16,17] of environmental benefits from organic farming is not meaningful in this case. However, trade-offs with other environmental effects, specifically GHG-emissions, which might increase by catch crops depending on the species [72,73], must be taken into account for a systemic sustainability evaluation, e.g., by calculating the total costs of nitrogen [74].

5. Conclusions

With this study, we could demonstrate that, already, moderately reduced N application rates can contribute to decreased NO_3 concentrations and lower cumulative leaching losses without significant yield depressions or quality effects. N losses were positively correlated with post-harvest SMN residuals. However, even without fertilisation, significant N leaching from soil mineralisation was observed. In highly vulnerable karst aquifers, this leads to tolerable N balance surpluses, below the limit of 50 kg ha⁻¹, as suggested from the

Agronomy **2021**, 11, 64 13 of 16

legal framework, since additionally replenishment from historical high inputs of organic fertilisers contribute to total leaching losses.

Supplementary Materials: The following are available online at https://www.mdpi.com/2073-439 5/11/1/64/s1, Figure S1: Estimation plot of NO₃-N concentrations and effect sizes for the individual crops.

Author Contributions: D.T. and I.K. conceptualised the study. M.B., M.V., and I.K. collected field data. M.V. and M.B. performed laboratory analyses. I.K. performed statistical analysis and data visualisation. I.K. and M.B. wrote the original draft. All authors contributed to review and editing and have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Ministry of Environment, Energy, and Climate Protection of Lower Saxony with support of the Water Management, Coastal Defence, and Nature Conservation Agency Lower Saxony (NLWKN) under sponsorship of Wittlage Water Association.

Acknowledgments: We thank our associated project partners from the Chamber of Agriculture Lower Saxony H. Siuts and the D. Bringewatt from the cooperation farm. For help with the field and laboratory work, we acknowledge M. Kohlbrecher, R. Opree, E. Nagel, and the experimental farm Waldhof. Furthermore, we would like to thank the three anonymous reviewers for their valuable comments on an earlier version of the manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

References

- 1. Zhang, X.; Davidson, E.A.; Mauzerall, D.L.; Searchinger, T.D.; Dumas, P.; Shen, Y. Managing nitrogen for sustainable development. *Nature* **2015**, *528*, 51–59. [PubMed]
- 2. Rockström, J.; Steffen, W.; Noone, K.; Persson, Å.; Chapin, F.S.; Lambin, E.F.; Lenton, T.M.; Scheffer, M.; Folke, C.; Schellnhuber, H.J.; et al. A safe operating space for humanity. *Nature* **2009**, *461*, 472–475. [CrossRef] [PubMed]
- 3. Steffen, W.; Richardson, K.; Rockström, J.; Cornell, S.E.; Fetzer, I.; Bennett, E.M.; Biggs, R.; Carpenter, S.R.; De Vries, W.; De Wit, C.A.; et al. Planetary boundaries: Guiding human development on a changing planet. *Science* **2015**, 347. [CrossRef]
- 4. Campbell, B.M.; Beare, D.J.; Bennett, E.M.; Hall-Spencer, J.M.; Ingram, J.S.I.; Jaramillo, F.; Ortiz, R.; Ramankutty, N.; Sayer, J.A.; Shindell, D. Agriculture production as a major driver of the Earth system exceeding planetary boundaries. *Ecol. Soc.* **2017**, 22, art8. [CrossRef]
- 5. Sutton, M.A.; Oenema, O.; Erisman, J.W.; Leip, A.; van Grinsven, H.; Winiwarter, W. Too much of a good thing. Nature 2011, 472, 159.
- 6. The Royal Society. Reaping the Benefits: Science and the Sustainable Intensification of Global Agriculture; RS Policy document 11/09; The Royal Society: London, UK, 2009.
- 7. Tilman, D.; Balzer, C.; Hill, J.; Befort, B.L. Global food demand and the sustainable intensification of agriculture. *Proc. Natl. Acad. Sci. USA* **2011**, *108*, 20260–20264. [CrossRef]
- 8. Tilman, D.; Cassman, K.G.; Matson, P.A.; Naylor, R.; Polasky, S. Agricultural sustainability and intensive production practices. *Nature* **2002**, *418*, 671–677. [CrossRef]
- 9. Foley, J.A.; DeFries, R.; Asner, G.P.; Barford, C.; Bonan, G.; Carpenter, S.R.; Chapin, F.S.; Coe, M.T.; Daily, G.C.; Gibbs, H.K.; et al. Global Consequences of Land Use. *Science* **2005**, *309*, 570–574. [CrossRef]
- 10. LBEG NIBIS Map Server–Soil Map Lower Saxony (BÜK50). Available online: https://nibis.lbeg.de/cardomap3/ (accessed on 5 September 2019).
- 11. Di, H.J.; Cameron, K.C. Nitrate leaching in temperate agroecosystems: Sources, factors and mitigating strategies. *Nutr. Cycl. Agroecosyst.* **2002**, *64*, 237–256. [CrossRef]
- 12. Meissner, R.; Rupp, H.; Seeger, J.; Schonert, P. Influence of mineral fertilizers and different soil types on nutrient leaching: Results of lysimeter studies in East Germany. *Land Degrad. Dev.* **1995**, *6*, 163–170. [CrossRef]
- 13. Köhler, K.; Duynisveld, W.H.M.; Böttcher, J. Nitrogen fertilization and nitrate leaching into groundwater on arable sandy soils. *J. Plant Nutr. Soil Sci.* **2006**, *169*, 185–195. [CrossRef]
- 14. Robertson, G.P.; Vitousek, P.M. Nitrogen in agriculture: Balancing the cost of an essential resource. *Annu. Rev. Environ. Resour.* **2009**, *34*, 97–125. [CrossRef]
- 15. IPCC. N₂O Emissions From Managed Soils, and CO₂ Emissions From Lime and Urea Application. In 2019 Refinement to the 2006 IPCC Guidelines for National Greenhouse Gas Inventories; IPCC: Geneva, Switzerland, 2019; pp. 1–48. ISBN 4887880324.
- 16. Schipanski, M.E.; Barbercheck, M.; Douglas, M.R.; Finney, D.M.; Haider, K.; Kaye, J.P.; Kemanian, A.R.; Mortensen, D.A.; Ryan, M.R.; Tooker, J.; et al. A framework for evaluating ecosystem services provided by cover crops in agroecosystems. *Agric. Syst.* **2014**, 125, 12–22. [CrossRef]
- 17. Zhou, M.; Butterbach-Bahl, K. Assessment of nitrate leaching loss on a yield-scaled basis from maize and wheat cropping systems. *Plant Soil* **2014**, *374*, *977*–*991*. [CrossRef]

Agronomy 2021, 11, 64 14 of 16

18. Delin, S.; Stenberg, M. Effect of nitrogen fertilization on nitrate leaching in relation to grain yield response on loamy sand in Sweden. *Eur. J. Agron.* **2014**, *52*, 291–296. [CrossRef]

- 19. Sanders, J.; Hess, J. Leistungen des ökologischen Landbaus für Umwelt und Gesellschaft, Thünen Rep 65; Sanders, J., Heß, J., Eds.; Johann Heinrich von Thünen-Institut: Braunschweig, Germany, 2019; ISBN 9783865761934.
- 20. EC European Parliament & Council. Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy. *OJL* **2000**, 327, 1–73.
- 21. EC. European Commission: Report on the Implementation of Council Directive 91/676/EEC Concerning the Protection of Waters against Pollution Caused by Nitrates from Agricultural Sources Based on Member State Reports for the Period 2012-2015; European Commission: Brussels, Belgium, 2018.
- 22. Vitousek, P.M.; Naylor, R.; Crews, T.; David, M.B.; Drinkwater, L.E.; Holland, E.; Johnes, P.J.; Katzenberger, J.; Martinelli, L.A.; Matson, P.A.; et al. Nutrient imbalances in agricultural development. *Science* **2009**, *324*, 1519–1520. [CrossRef]
- 23. DüV Düngeverordnung vom 26. Mai 2017 (BGBl. I S. 1305), die durch Artikel 1 der Verordnung vom 28. April 2020 (BGBl. I S. 846) geändert worden ist-German Fertiliser Ordinance. Available online: https://www.gesetze-im-internet.de/d_v_2017/index.html (accessed on 1 May 2020).
- 24. Hülsbergen, K.-J. Entwicklung und Anwendung eines Bilanzierungsmodells zur Bewertung der Nachhaltigkeit landwirtschaftlicher Systeme; Shaker: Aachen, Germany, 2003; ISBN 3-8322-1464-X.
- 25. Lord, E.I.; Mitchell, R.D.J. Effect of nitrogen inputs to cereals on nitrate leaching from sandy soils. *Soil Use Manag.* **1998**, *14*, 78–83. [CrossRef]
- 26. Goulding, K. Nitrate leaching from arable and horticultural land. Soil Use Manag. 2000, 16, 145–151. [CrossRef]
- 27. Billen, G.; Garnier, J.; Némery, J.; Sebilo, M.; Sferratore, A.; Barles, S.; Benoit, P.; Benoît, M. A long-term view of nutrient transfers through the Seine river continuum. *Sci. Total Environ.* **2007**, *375*, 80–97. [CrossRef]
- 28. Ying, H.; Ye, Y.; Cui, Z.; Chen, X. Managing nitrogen for sustainable wheat production. *J. Clean. Prod.* **2017**, *162*, 1308–1316. [CrossRef]
- 29. Wang, Y.; Ying, H.; Yin, Y.; Zheng, H.; Cui, Z. Estimating soil nitrate leaching of nitrogen fertilizer from global meta-analysis. *Sci. Total Environ.* **2019**, 657, 96–102. [CrossRef] [PubMed]
- 30. Yin, Y.; Ying, H.; Xue, Y.; Zheng, H.; Zhang, Q.; Cui, Z. Calculating socially optimal nitrogen (N) fertilization rates for sustainable N management in China. *Sci. Total Environ.* **2019**, *688*, 1162–1171. [CrossRef] [PubMed]
- 31. Tonitto, C.; David, M.B.B.; Drinkwater, L.E.E. Replacing bare fallows with cover crops in fertilizer-intensive cropping systems: A meta-analysis of crop yield and N dynamics. *Agric. Ecosyst. Environ.* **2006**, *112*, 58–72. [CrossRef]
- 32. Abdalla, M.; Hastings, A.; Cheng, K.; Yue, Q.; Chadwick, D.; Espenberg, M.; Truu, J.; Rees, R.M.; Smith, P. A critical review of the impacts of cover crops on nitrogen leaching, net greenhouse gas balance and crop productivity. *Glob. Chang. Biol.* **2019**, 25, 2530–2543. [CrossRef]
- 33. Constantin, J.; Mary, B.; Laurent, F.; Aubrion, G.; Fontaine, A.; Kerveillant, P.; Beaudoin, N. Effects of catch crops, no till and reduced nitrogen fertilization on nitrogen leaching and balance in three long-term experiments. *Agric. Ecosyst. Environ.* **2010**, *135*, 268–278. [CrossRef]
- 34. Quemada, M.; Baranski, M.; Nobel-de Lange, M.N.J.; Vallejo, A.; Cooper, J.M. Meta-analysis of strategies to control nitrate leaching in irrigated agricultural systems and their effects on crop yield. *Agric. Ecosyst. Environ.* **2013**, *174*, 1–10. [CrossRef]
- 35. Trenkel, M.E. Controlled-Release and Stabilized Fertilizers in Agriculture; IFA: Paris, France, 1997; ISBN 2-9506299-0-3.
- 36. Benoit, M.; Josette, G.; Gilles, B.; Julien, T.; Eric, G.; Bruno, M. Nitrous oxide emissions and nitrate leaching in an organic and a conventional cropping system (Seine basin, France). *Agric. Ecosyst. Environ.* **2015**, 213, 131–141. [CrossRef]
- 37. Hansen, B.; Steen, E.; Grant, R.; Høgh-Jensen, H.; Erik, S.; Olesen, J.E.; Kristensen, E.S.; Grant, R.; Høgh-Jensen, H.; Simmelsgaard, S.E.; et al. Nitrogen leaching from conventional versus organic farming systems—A systems modelling approach. *Eur. J. Agron.* 2000, *13*, 65–82. [CrossRef]
- 38. Benoit, M.; Garnier, J.; Beaudoin, N.; Billen, G. A participative network of organic and conventional crop farms in the Seine Basin (France) for evaluating nitrate leaching and yield performance. *Agric. Syst.* **2016**, *148*, 105–113. [CrossRef]
- 39. Stopes, C.; Lord, E.I.; Philipps, L.; Woodward, L. Nitrate leaching from organic farms and conventional farms following best practice. *Soil Use Manag.* **2002**, *18*, 256–263. [CrossRef]
- 40. Askegaard, M.; Olesen, J.E.; Rasmussen, I.A.; Kristensen, K. Nitrate leaching from organic arable crop rotations is mostly determined by autumn field management. *Agric. Ecosyst. Environ.* **2011**, *142*, 149–160. [CrossRef]
- 41. De Notaris, C.; Rasmussen, J.; Sørensen, P.; Olesen, J.E. Nitrogen leaching: A crop rotation perspective on the effect of N surplus, field management and use of catch crops. *Agric. Ecosyst. Environ.* **2018**, 255, 1–11. [CrossRef]
- 42. Bender, S.F.; van der Heijden, M.G.A. Soil biota enhance agricultural sustainability by improving crop yield, nutrient uptake and reducing nitrogen leaching losses. *J. Appl. Ecol.* **2015**, *52*, 228–239. [CrossRef]
- 43. Henneron, L.; Bernard, L.; Hedde, M.; Pelosi, C.; Villenave, C.; Chenu, C.; Bertrand, M.; Girardin, C.; Blanchart, E. Fourteen years of evidence for positive effects of conservation agriculture and organic farming on soil life. *Agron. Sustain. Dev.* **2014**, *35*, 169–181. [CrossRef]
- 44. Boumans, L.J.M.; Fraters, D.; Van Drecht, G. Nitrate leaching in agriculture to upper groundwater in the sandy regions of the Netherlands during the 1992–1995 period. *Environ. Monit. Assess.* **2005**, *102*, 225–241. [CrossRef] [PubMed]
- 45. Bakalowicz, M. Karst groundwater: A challenge for new resources. Hydrogeol. J. 2005, 13, 148–160. [CrossRef]

Agronomy **2021**, 11, 64 15 of 16

46. Peel, M.C.; Finlayson, B.L.; McMahon, T.A. Updated world map of the Köppen-Geiger climate classification. *Hydrol. Earth Syst. Sci.* **2007**, *11*, 1633–1644. [CrossRef]

- 47. DWD. Deutscher Wetterdienst: Climate Dataset—Archive Data Station 342 Belm. Available online: http://www.dwd.de (accessed on 20 June 2020).
- 48. FAO. World Reference Base for Soil Resources 2014 International Soil Classification System for Naming Soils and Creating Legends for Soil Maps—Update 2015; FAO: Rome, Italy, 2015; ISBN 9789251083697/925108369X.
- 49. VDLUFA. Determination of mineral nitrogen (nitrate and ammonium) in soil profiles (Nmin laboratory method. In *Bestimmung von Mineralischem Stickstoff (Nitrat und Ammonium) in Bodenprofilen (Nmin-Labormethode A 6.1.4.1)*; VDLUFA: Darmstadt, Germany, 2002. (In German)
- 50. VDLUFA. Determination of nitrate nitrogen by UV absorption (nitrate nitrogen (UV absorption). In *Bestimmung von Nitrat-Stickstoff durch UV-Absorption (Nitrat-Stickstoff (UV-Absorption) A 6.1.1.1)*; VDLUFA: Darmstadt, Germany, 2002. (In German)
- 51. Engel, N.; Müller, U.; Schäfer, W. BOWAB—Ein Mehrschicht-Bodenwasserhaushaltsmodell. In *GeoBerichte 20: Klimawandel und Bodenwasserhaushalt*; LBEG, Ed.; LBEG: Hannover, Germany, 2012; pp. 85–98.
- 52. Trautz, D.; Beiküfner, M.; Vergara, M.; Kühling, I.; Siuts, H.; Müller, S. Modell-und Pilotprojekt zur Ermittlung von Grundlagen für die Umsetzung ordnungsrechtlicher Stickstoffdüngungsbeschränkungen am Beispiel des Wasserschutzgebietes Belm-Nettetal im Landkreis Osnabrück. *NLWKN Grund. R.* **2020**, *44*, 1–69.
- 53. R Core Team. R: A Language and Environment for Statistical Computing R. Foundation for Statistical Computing Version 4.0.2. Available online: http://www.r-project.org/ (accessed on 22 June 2020).
- 54. de Mendiburu, F. Agricolae: Statistical Procedures for Agricultural Research. Available online: http://cran.r-project.org/package=agricolae (accessed on 6 September 2020).
- 55. Ho, J.; Tumkaya, T.; Aryal, S.; Choi, H.; Claridge-Chang, A. Moving beyond P values: Data analysis with estimation graphics. *Nat. Methods* **2019**, *16*, 565–566. [CrossRef]
- 56. Ho, J.; Tumkaya, T. Dabestr: Data Analysis Using Bootstrap-Coupled Estimation. Available online: https://github.com/ACCLAB/dabestr (accessed on 14 September 2020).
- 57. Sieling, K. Growth stage-specific application of slurry and mineral N to oilseed rape, wheat and barley. *J. Agric. Sci.* **2004**, *142*, 495–502. [CrossRef]
- 58. Heumann, S.; Fier, A.; Haßdenteufel, M.; Höper, H.; Schäfer, W.; Eiler, T.; Böttcher, J. Minimizing nitrate leaching while maintaining crop yields: Insights by simulating net N mineralization. *Nutr. Cycl. Agroecosyst.* **2013**, *95*, 395–408. [CrossRef]
- 59. Kayser, M.; Benke, M.; Isselstein, J. Little fertilizer response but high N loss risk of maize on a productive organic-sandy soil. *Agron. Sustain. Dev.* **2011**, *31*, 709–718. [CrossRef]
- 60. Stehfest, E.; Bouwman, L. N2O and NO emission from agricultural fields and soils under natural vegetation: Summarizing available measurement data and modeling of global annual emissions. *Nutr. Cycl. Agroecosyst.* **2006**, 74, 207–228. [CrossRef]
- 61. Lin, B.L.; Sakoda, A.; Shibasaki, R.; Suzuki, M. A modelling approach to global nitrate leaching caused by anthropogenic fertilisation. *Water Res.* **2001**, *35*, 1961–1968. [CrossRef]
- 62. Simmelsgaard, S.E.; Djurhuus, J. An empirical model for estimating nitrate leaching as affected by crop type and the long-term N fertilizer rate. *Soil Use Manag.* **1998**, *14*, 37–43. [CrossRef]
- 63. Wachendorf, M.; Volkers, K.C.; Loges, R.; Rave, G.; Taube, F. Performance and environmental effects of forage production on sandy soils. IV. Impact of slurry application, mineral N fertilizer and grass understorey on yield and nitrogen surplus of maize for silage. *Grass Forage Sci.* 2006, 61, 232–242. [CrossRef]
- 64. Cookson, W.R.; Rowarth, J.S.; Cameron, K.C. The effect of autumn applied 15N-labelled fertilizer on nitrate leaching in a cultivated soil during winter. *Nutr. Cycl. Agroecosystems* **2000**. [CrossRef]
- 65. Teixeira, E.I.; Johnstone, P.; Chakwizira, E.; de Ruiter, J.; Malcolm, B.; Shaw, N.; Zyskowski, R.; Khaembah, E.; Sharp, J.; Meenken, E.; et al. Sources of variability in the effectiveness of winter cover crops for mitigating N leaching. *Agric. Ecosyst. Environ.* **2016**, 220, 226–235. [CrossRef]
- 66. Mehranfar, O. Laboruntersuchungen zum langfristigen Denitrifikationspotential im oberflächennahen Grundwasser hydromorpher Mineralböden Nordwestdeutschlands. Ph.D. Thesis, University Göttingen, Göttingen, Germany, 2003.
- 67. Wong, M.T.F.; Asseng, S.; Zhang, H. Precision agriculture improves efficiency of nitrogen use and minimises its leaching at within-field to farm scales. *Precis. Agric.* 2005 ECPA **2005**, 969–976.
- 68. Banger, K.; Wagner-Riddle, C.; Grant, B.B.; Smith, W.N.; Drury, C.; Yang, J. Modifying fertilizer rate and application method reduces environmental nitrogen losses and increases corn yield in Ontario. *Sci. Total Environ.* **2020**, 722, 137851. [CrossRef] [PubMed]
- 69. Stadtwerke Leipzig Wassergut Canitz. Available online: https://www.l.de/gruppe/das-sind-wir/leipziger-gruppe/wassergut-canitz (accessed on 26 November 2020).
- 70. Stadtwerke München Ökologischer Landbau | Initiative Ökobauern. Available online: https://www.swm.de/wasser/trinkwasserschutz/oekologischer-landbau (accessed on 26 November 2020).
- 71. Biernat, L.; Taube, F.; Vogeler, I.; Reinsch, T.; Kluß, C.; Loges, R. Is organic agriculture in line with the EU-Nitrate directive? On-farm nitrate leaching from organic and conventional arable crop rotations. *Agric. Ecosyst. Environ.* **2020**, 298, 106964. [CrossRef]

Agronomy **2021**, 11, 64 16 of 16

72. Poeplau, C.; Don, A. Carbon sequestration in agricultural soils via cultivation of cover crops–A meta-analysis. *Agric. Ecosyst. Environ.* **2015**, 200, 33–41. [CrossRef]

- 73. Basche, A.D.; Miguez, F.E.; Kaspar, T.C.; Castellano, M.J. Do cover crops increase or decrease nitrous oxide emissions? A meta-analysis. *J. Soil Water Conserv.* **2014**, *69*, 471–482. [CrossRef]
- 74. Van Grinsven, H.J.M.; Holland, M.; Jacobsen, B.H.; Klimont, Z.; Sutton, M.A.; Jaap Willems, W. Costs and benefits of nitrogen for europe and implications for mitigation. *Environ. Sci. Technol.* **2013**, *47*, 3571–3579. [CrossRef] [PubMed]