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Mismatches between ammonium and nitrate losses at the field and watershed scales suggest contrasting controls in two agricultural watersheds

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ABSTRACT

Nitrogen (N) fertilizer enhances crop production, but field runoff impacts water quality in adjacent freshwaters. Planting winter cover crops reduces nitrate-N losses during the fallow period, but less is known about impacts on ammonium-N. From 2016–2023, we sampled biweekly from the Shatto Ditch and Kirkpatrick Ditch Watersheds in Indiana (USA) to compare the impact of cover crops on dissolved inorganic nitrogen at the field-, edge-of-field, and watershed-scales. We measured soil ammonium-N and nitrate-N, biomass, and organic matter in fall and spring. Cover crops reduced soil ammonium-N at Shatto and soil nitrate-N in both watersheds. Tile losses and watershed yields of ammonium-N occurred on scales orders of magnitude lower than nitrate-N. Tile ammonium-N losses from cover cropped fields ranged from 97 % lower to 31 % higher at Shatto, and 45 % lower to 75 % higher at Kirkpatrick compared to those without. Cover crops reduced field-scale nitrate-N losses at Shatto by 58–87 %, but losses at Kirkpatrick ranged 99 % lower to 15 % higher. Tile flow explained interannual variation in nitrate-N losses, while field-scale ammonium-N losses were driven by soil and microbial interactions and mobilization during storms. Watershed-scale ammonium-N and nitrate-N yields correlated with runoff (Kendall τ=0.45 and 0.39, respectively). While nitrate-N yields mirrored runoff, ammonium-N yields exhibited a step-functional increase, pointing to the importance of storms as a driver of loss. As Midwest crop production adapts to fluctuating environmental conditions, we demonstrate how applying cover crops over a multi-year period can mitigate ammonium-N losses.

1. Introduction

Nitrogen (N) fertilizer is used ubiquitously across the agricultural Midwest to increase crop yields and is commonly applied as urea or anhydrous ammonia (Bierman et al., 2012; Turner and Rabalais, 1991). Anhydrous ammonia reacts with water to become ammonium (NH_4^+-N), subsequently adhering to soils or being rapidly assimilated into plant biomass (Griesheim et al., 2023; Sawyer, 2019). In addition, NH_4^+-N on fields can be transformed into nitrate (NO_3^--N) via the process of nitrification (Norton and Ouyang, 2019; Tortoso and Hutchinson, 1990), or it can be transported into adjacent waterways. The export of NO_3^--N from agricultural landscapes is well documented (David et al., 1997; Royer et al., 2006; Williams et al., 2015), and patterns have previously been linked to excess fertilizer application, combined with significant modification associated with landscape drainage (Gentry et al., 1998; Jaynes et al., 1999), precipitation, and associated runoff (Hanrahan et al., 2018; Logan et al., 1994). Furthermore, NO_3^--N export from agricultural landscapes is exacerbated by the occurrence of storms (Speir et al., 2021; Vaughan et al., 2017). Compared to NH_4^+-N, which adsorbs easily to soil particles, NO_3^--N export correlates with runoff and is closely linked to watershed hydrology (Kaushal et al., 2011; Royer et al., 2006). Excess NO_3^--N from the midwestern USA is the primary source of N pollution to the Mississippi River, contributing up to 45 % of the N flux that reaches the Gulf of Mexico (David et al., 2010; Rabalais et al., 2002). The

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majority of these N losses occur during the fallow period after cash crop harvest, during winter and spring (Speir et al., 2022). Given the biogeochemical linkage between NH_4^+-N and NO_3^--N via the process of nitrification, which can occur in agricultural soils (Robertson et al., 2013; Tortoso and Hutchinson, 1990) or after NH_4^+-N enters aquatic systems (Kemp and Dodds, 2002), documenting the drivers of NH_4^+-N losses from fields and stream export during the fallow period is critical to understand a component of N cycling in agroecosystems that is comparatively understudied.

Low-gradient, agricultural lands in the midwestern US are managed for effective drainage via the installation of subsurface tile drains, which have been maintained on up to 70 million acres across the Mississippi River basin (Blann et al., 2009). Subsurface tile drains expedite the transport of nutrient-rich waters from the landscape to adjacent streams and ditches, circumventing riparian buffers, and any potential nutrient removal processes (Blann et al., 2009; King et al., 2014; Ranalli and Macalady, 2010). In addition to the inputs from subsurface tile drainage, routine channelization and removal of riparian vegetation reduces the hydraulic residence time in agricultural streams, sustaining these open-canopy headwaters as high throughput (i.e., shunt) systems, resulting in effective transport of dissolved nutrients to downstream ecosystems which is highest during high flow events (Raymond et al., 2016; Speir et al., 2022). Under current climate projections, the intensity and frequency of storms in Indiana and across the agricultural Midwest are projected to increase (Hamlet et al., 2020; USGCRP, 2017). This increase in precipitation is anticipated to occur across much of the United States. While the Pacific Northwest and Plains regions are expected to receive more rainfall in the spring and summer, respectively, the Midwest is expected to be impacted throughout the year (USGCRP, 2017). This shift in rainfall is closely aligned with increasing temperatures, and an earlier snowmelt period. In Indiana, more rain is expected to fall during the colder months (i.e., November to March), including rain on snow, and warming spring temperatures will bring heavy rainfall events, and not snow, earlier in the year (Hamlet et al., 2020; Widhalm et al., 2018). Additionally, the occurrence of stronger precipitation earlier in the year will facilitate higher rates of nutrient export to downstream ecosystems (Hamlet et al., 2024; Richards and Baker, 2002; Royer et al., 2006).

Planting winter cover crops (CC) after cash crop harvest provides living coverage during the fallow season when agricultural fields are typically left bare, and are most susceptible to nutrient losses (e.g., snowmelt, storms; Kaspar et al., 2012, 2007; Lacey and Armstrong, 2015). The efficacy of CC as a conservation practice to limit nutrient loss has been well-studied at the landscape scale and has been shown to be effective at limiting losses of NO_3^--N (Hanrahan et al., 2018; Qi et al., 2011; Speir et al., 2022) and soluble reactive phosphorus (SRP; Daryanto et al., 2018; Norberg and Aronsson, 2020; Trentman et al., 2020), in addition to improving soil health (Basche and DeLonge, 2019; Blanco-Canqui et al., 2015; Christopher et al., 2021), and preventing erosion (Dabney et al., 2001). Despite these promising results at the field-scale, watershed-scale reductions can be obscured by nutrients entering streams via groundwater inputs (Grose et al., 2022) or via expansive county tile drains which incorporate additions from outside watershed boundaries (Speir et al., 2022). Previous work has shown that winter CC can potentially reduce soil NH_4^+-N (Christopher et al., 2021), which may reduce edge-of-field-scale NH_4^+-N losses from tile drains during the winter and spring seasons and deserves further exploration.

Despite the intense focus and documentation of the downstream damages of excess N export (Goolsby et al., 1999; Rabalais et al., 2002; Van Meter et al., 2018) and the critical need for effective conservation practice implementation at in the Midwestern region (Alexander et al., 2008), the effects of CC on field- and watershed-scale NH_4^+-N dynamics are not well-documented. Inputs of NH_4^+-N from the surrounding landscape can potentially undergo in-stream nitrification (Kemp and Dodds, 2002) and contribute to watershed NO_3^--N export (Bernot and Dodds, 2005; Dodds et al., 2000; Peterson et al., 2001). As climate change alters key drivers of nutrient loss in midwestern watersheds, such as precipitation patterns and the timing of spring snowmelt (Hamlet et al., 2020; USGCRP, 2017), accurate documentation of the effects CC on NH_4^+-N transport in agricultural watersheds is warranted, because NH_4^+-N export has the potential to contribute to NO_3^--N export via the process of nitrification in soils and adjacent aquatic environments (Kemp and Dodds, 2002; Norton and Ouyang, 2019).

This study contributes to the ongoing Indiana Watershed Initiative (IWI) project, where we have been quantifying the impacts of agricultural conservation practices (e.g., CC and two-stage floodplain restoration) on soil health (Christopher et al., 2021) and the mitigation of N and phosphorous (P) losses at the field- and watershed-scale in working landscapes (Grose et al., 2022; Hanrahan et al., 2018; Sethna et al., 2022; Speir et al., 2022; Tank et al., 2021; Trentman et al., 2020). Prior work has demonstrated that planting winter CC reduces the pool of N and P that can be transported from fields into adjacent waterways, and that even minor increases in CC biomass are related to 50–90 % reductions in soil NO_3^--N (Christopher et al., 2021). Furthermore, planting winter CC can reduce field-scale NO_3^--N and SRP losses by 27–72 % and 7–59 %, respectively, and are effective across a range of precipitation conditions (Hanrahan et al., 2018; Speir et al., 2022; Trentman et al., 2020). Patterns at the watershed-scale, however, ranged from a 20 % decrease to a 110 % increase (Speir et al., 2022), demonstrating that drivers of nutrient loss may vary across spatiotemporal scales, even within the same system. In this study, we use long-term data ($n = 7–8$ years) from two agriculturally dominated watersheds to quantify the effect of CC on mitigating field-scale NH_4^+-N losses from tile drains, and we examine patterns of watershed-scale export, thus elucidating a component of N cycling in agroecosystems that has not been well documented. Here, we compare field- and watershed-scale results for NH_4^+-N to NO_3^--N to explore linkages in the transport of these solutes in working agricultural landscapes, and to determine if land cover alters field, edge-of-field, and watershed-scale losses.

Here, field-scale measurements include those taken directly from the soil and cover crop biomass. The edge-of-field scale includes losses recorded from tile drains while the watershed-scale captures the export from the stream outlet. At the field-scale, we hypothesized that CC would effectively assimilate NH_4^+-N into CC biomass or soil organic N, thus reducing edge-of-field NH_4^+-N losses and altering dissolved inorganic nitrogen (DIN; NO_3^--N + NH_4^+-N) stoichiometry from tile drains compared to fields left fallow after harvest. At the watershed-scale, we predicted that increased CC coverage in the two study watersheds would result in lower NH_4^+-N yields during the fallow season when CC biomass is actively growing, the magnitude of NH_4^+-N export would be much lower compared to NO_3^--N due to preferential NH_4^+-N removal by aquatic biota and tight biogeochemical cycling (Mulholland et al., 2008; Tank and Dodds, 2003), and the timing of NH_4^+-N and NO_3^--N export would mirror one another and be linked to high flow conditions (i.e., storms) when increased flows mobilize NO_3^--N and NH_4^+-N adsorbed to soils or stream sediments (Chen et al., 2018; Royer et al., 2006).

2. Materials and methods

2.1. Study sites

As part of the long-term IWI project (Hanrahan et al., 2018; Speir et al., 2022; Trentman et al., 2020), we sampled two watersheds in northern Indiana dominated by row-crop agriculture: the Shatto Ditch Watershed (referred to as “Shatto”, hereafter; Kosciusko County) and Kirkpatrick Ditch Watershed (referred to as “Kirkpatrick”, hereafter; divided by Jasper, Benton, and Newton Counties). Both watersheds are small, Shatto = 1333 hectares (ha) and Kirkpatrick = 2630 ha, and both watersheds are actively farmed by independent producers in a corn-soybean rotation (>85 %; Hanrahan et al., 2018; Trentman et al., 2020), making these two sites representative of other working lands in the midwestern US (Fig. 1). During the study period, at Shatto, air

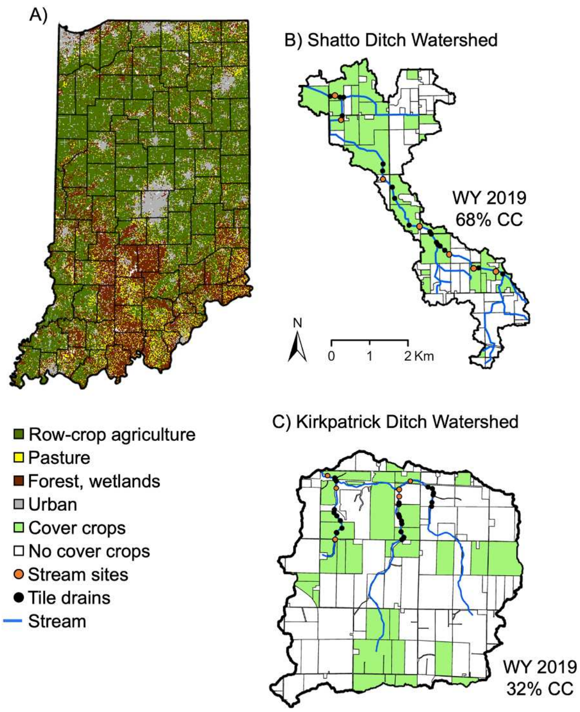

Fig. 1. A) State map of Indiana with land cover information adapted from the USGS National Land Cover Database (USGS, 2018). Detailed maps of B) Shatto Ditch Watershed (Shatto) and C) Kirkpatrick Ditch Watershed (Kirkpatrick) in north-central Indiana, USA. We sampled tile drains (black points) and stream sites (orange points) biweekly from water year 2016–2023 (water year 2022 at Kirkpatrick). Green on watershed maps denotes CC distribution during water year 2019 and represents the peak coverage achieved for both watersheds during the study period. The scale bar corresponds to the two watershed maps in panels (B) and (C).

temperatures ranged from −21–30°C with a grand mean of 11 ± 0.2°C over the study period, total precipitation ranged from 429 to 1098 mm, and total runoff ranged from 205 to 616 mm (Fig. S1A,C,E). At Kirkpatrick, air temperatures ranged from −24–31°C with a grand mean of 11 ± 0.2°C over the study period, total precipitation ranged from 429 to 1098 mm, and total runoff ranged from 282 to 488 mm (Fig. S1B,D,F).

The watersheds have similar topographical features including poorly drained soils and low topographic relief. In the Shatto, soils are primarily Alfisols (77 %) and Mollisols (13 %) with a texture of sandy loam, loam, and muck (Christopher et al., 2021). It is estimated that up to 79 % of land at Shatto is underlain with subsurface tile drains (Gökkaya et al., 2017), and over 12 years of monitoring we see very few overland flow events during storms (<5 times over the multi-year study). At Kirkpatrick, soils are Mollisols with a silty clay loam texture (Christopher et al., 2021; USDA, 2020), and tile drains extend from most fields adjacent to the stream, although exact tile drain coverage for Kirkpatrick is unknown (Trentman et al., 2020), and overland flow was also rare (<10 times days during the study). Tillage practices vary between the two watersheds. No-till and conservation tillage practices predominate at Shatto, while for Kirkpatrick, conventional tillage is used on 60 % of fields, with a mix of conservation and no-till on the remaining fields (Speir et al., 2022). Most producers in both watersheds apply inorganic N fertilizer as a spring starter with an additional side dress in early summer, and while manure application is uncommon at Shatto occur occasionally on select fields at Kirkpatrick in the autumn (J. T., *personal communication*).

This project is a continuation of work that evaluated the role of CC coverage on soil N and phosphorus (P; Christopher et al., 2021) and tile drain NO_3^--N and SRP losses (Hanrahan et al., 2018; Speir et al., 2022; Trentman et al., 2020). Briefly, we provided producers with incentive funding to plant CC after crop harvest during the 2016–2019 water years (12-month period Oct 1-Sept 30). The incentives resulted in CC coverage on 62–68 % of croppable area in Shatto and 12–32 % in Kirkpatrick over the 2016–2019 water years. Although producers were obligated to follow Natural Resources Conservation Service guidelines to maintain eligibility, we did not specify CC species or any other changes to land management. The CC species planted varied over the course of the study with producers planting mostly annual ryegrass (*Lolilium multiflorum* Lam.) and cereal rye (*Secale cereal* L.). We also documented a few instances of winter wheat (*Triticum aestivum*) and a mix of oats (*Avena sativa*) and radish (*Raphanus sativus L.* var. *niger J. Kern*), although this was rare. Cereal and annual rye is terminated in spring using either herbicide or tillage approximately two weeks before planting cash crops while winter wheat is harvested in autumn, and the oats-radish mix is "winter-killed" by freezing temperatures. Distribution of incentives ended after water year 2019, and CC coverage in the watersheds subsequently declined to 21–35 % at Shatto and 8–12 % at Kirkpatrick (Table 1). We maintained a record of percent CC coverage in each watershed for the duration of the study period, which we calculated based on windshield surveys conducted in each watershed in autumn and spring. For context, CC coverage on croppable acres stands at 14 % for Indiana (ISDA, 2023) and at 7 % across the midwestern Corn Belt (Zhou et al., 2022).

2.2. Sampling regime

We analyzed a large dataset of biannual soils data and biweekly water chemistry monitoring data for eight years for Shatto (water years 2016–2023) and seven years for Kirkpatrick (water years 2016–2022). Following methods described by Christopher et al. (2021), we collected soils and CC biomass from each watershed twice per year, once in the fall after crop harvest (October-December) and again in the spring before CC termination and cash crop planting (March-April). Briefly, we collected replicate soil cores from two depths (0–5 cm and 5–20 cm) from fields with and without CC throughout each watershed; when present, we also sampled aboveground CC biomass (0.3 m^2 quadrat). For this analysis, we include soil and CC biomass data from soil sampling fields for which we also have data from the corresponding underlain tile drain (n = 6 at Shatto and n = 3 at Kirkpatrick). We analyzed soils for NH_4^+-N and NO_3^--N content (Dahnke, 1990), and organic matter content (Schulte and Hopkins, 1996). For these analyses, due to their similarity, we pooled soil data across the two sampling depths.

For water sampling, we collected grab samples from n = 22 tile drains and n = 7 stream sites at Shatto, and n = 20 tile drains and n = 6 stream sites at Kirkpatrick twice per month from water years 2016–2023 (Fig. 1). For this analysis, we have included only tiles that drain a single field (diameter <0.3 m; Shatto: n = 17, Kirkpatrick: n = 18), while larger "county" tiles draining a larger land area have been excluded (Speir et al., 2022). We classified each drain as "CC" or "no CC" based on the field coverage for that water year. On each sampling date, we collected triplicate water samples from each stream site and tile drain, and we analyzed each water sample for dissolved NH_4^+-N and NO_3^--N using the phenol-hypochlorite (Solórzano, 1969) and cadmium reduction methods (APHA, 2017), respectively, on a Lachat Flow Injection Auto-analyzer (Lachat Instruments, Loveland, CO, USA). With each grab sample, we also measured specific conductivity (μS cm^{-1}), pH, water temperature (°C), and turbidity (NTU). We maintain a record of continuous discharge (Q) using a US Geological Survey (USGS) gauge installed at the Shatto outlet (gauge #3331224) and have a record of continuous Q for Kirkpatrick spanning the sample collection period (gauge #5524546). For tile drains, we measured instantaneous flow using a graduated bucket and stopwatch, repeating measurements a minimum of n = 3 times for consistency. For instances of high flow (>10 L s^{-1}), we measured tile drain water velocity with a Marsh-McBirney Flo-Mate flow meter (Danaher Corporation; Washington, D.C., USA) and calculated tile Q using the following equations:

Table 1
Summary of site characteristics and watershed-scale NH_4^+-N and NO_3^--N export for the fallow season (October 1 to May 15) of each study year. Sampling at Kirkpatrick stopped after water year 2022. Percent cover crop (CC) coverage was calculated as proportion of croppable area planted with CC.

	Water Year	CC Coverage (%)	Runoff (mm)	NH_4^+-N Export (kg)	NH_4^+-N Yield (kg ha^{-1})	NO_3^--N Export (kg)	NO_3^--N Yield (kg ha^{-1})
Shatto Ditch Watershed	**2016**	68	258	124	0.1	20373	15.3
	2017	62	349	635	0.5	32626	24.5
	2018	62	494	946	0.7	31443	23.6
	2019	68	386	410	0.3	32600	24.5
	2020	23	318	211	0.2	20776	15.6
	2021	35	79	255	0.2	5455	4.1
	2022	30	356	521	0.4	28202	21.2
	2023	21	172	91	0.1	14675	11.0
Kirkpatrick Ditch Watershed	**2016**	23	242	176	0.1	64204	24.4
	2017	24	280	151	0.1	85802	32.6
	2018	13	290	209	0.1	59759	22.7
	2019	32	375	170	0.1	70567	26.8
	2020	12	219	44	0.02	51578	19.6
	2021	11	152	13	0.005	47330	18.0
	2022	8	270	704	0.3	81893	31.1

$$\theta = \left(1 - \frac{d}{r}\right)$$

$$Q_{TD} = r^2(\theta - \cos\theta\sin\theta) * v * 1000$$

where d is water depth measured at the outlet of the tile (m), r is the tile drain radius (m), v is water velocity, and Q_{TD} is tile drain Q (L s^{-1}). During high flow events, we did not collect grab samples from submerged tile drains, as we could not control for stream contamination or accurately measure flow. We also excluded instances of no flow (e.g., dry during summer, frozen in winter) from this analysis (i.e., we did not assign a value of zero).

2.3. Data analysis

We explored controls on soil N content, as well as drivers of DIN losses from fields to waterways and watershed-scale export over multiple years. For tile drains, we estimated instantaneous losses (μg s^{-1}) on each sampling date by multiplying solute concentration (μg L^{-1}) and instantaneous Q (L s^{-1}). We calculated an NH_4^+-N:DIN ratio (DIN = NH_4^+-N concentration + NO_3^--N concentration) to examine the proportion of DIN lost from tile drains as NH_4^+-N, and we compared these ratios between fields with and without CC to determine if the addition of CC altered the stoichiometry of tile drain N losses during the fallow period. At the watershed-scale, we modeled stream NH_4^+-N and NO_3^--N loads (kg d^{-1}) at the outlets using the *Loadflex* package in R which estimates solute export from Q and nutrient concentration data (Appling et al., 2015). Inputs to the model include surface water NH_4^+-N or NO_3^--N concentrations from routine sampling dates and daily Q measured at watershed outlets via the installed USGS gauges. Following the methods from previously published work in our watersheds, we used the Loadflex *interpolation* model to estimate daily NH_4^+-N loads to account for the poor regression relationship between flow and NH_4^+-N concentration (Appling et al., 2015; Speir et al., 2022). To estimate daily NO_3^--N export, we used the Loadflex *composite* model, which uses the residuals of the concentration-Q regression to minimize differences between export estimates and observed data (Appling et al., 2015; Hanrahan et al., 2018; Speir et al., 2022). For direct comparison between Shatto and Kirkpatrick, we scaled load estimates by watershed area to calculate NH_4^+-N or NO_3^--N yields (kg ha $^{-1}$ d^{-1}). We used a flow duration analysis (FDA) to determine the proportion of NH_4^+-N or NO_3^--N export occurring during the highest flows (i.e., storms). For the FDA, we ranked all study days from lowest to highest flows and categorized days as high (90 percentile and above), medium/mid (60–90th percentile), and low (<60 percentile). Finally, we calculated cumulative NH_4^+-N and NO_3^--N yields (kg ha^{-1}) over the water year and related cumulative yields to cumulative watershed runoff at the watershed outlet.

2.4. Statistical analysis

We performed all statistical analyses using R version 3.6.3 (R Core Team, 2021). We used two-way analysis of variance (ANOVA) to compare soil NH_4^+-N and NO_3^--N with CC treatment and cash crop planted during the prior growing season. We also compared the effects of CC treatment and season on soil NH_4^+-N and NO_3^--N, and tile NH_4^+-N and NO_3^--N losses using two-way ANOVA. Following a significant p value for our main effects and no interaction, we used Tukey's post hoc test to assess differences between treatments. We performed the non-parametric Mann-Whitney U Test to compare NH_4^+-N and NO_3^--N losses between tiles draining fields with and without CC because data failed the Shapiro-Wilk normality test, and normality could not be achieved using log10 or square root transformations. We used a Bonferroni correction to adjust the significance level to account for testing multiple years ($p = 0.05$/number of study years for each watershed). We used simple linear regression to assess the relationship between outlet and tile drain DIN concentrations, as well as the relationship between DIN export from the watershed outlets compared to the total DIN losses from tile drains on a given sampling date. We used Kendall's correlation to assess the level of association between NH_4^+-N or NO_3^--N yields and Q or runoff as possible drivers of watershed-scale dynamics.

3. Results

3.1. Cover crops influence soil chemistry

Overall, the two study watersheds had similar soil NH_4^+-N and NO_3^--N content (reported as mg kg^{-1}; *t*-test $p > 0.05$), and use of CC resulted in similar reductions in soil DIN content. At Shatto, we found that fields planted with CC had significantly lower soil NH_4^+-N compared to those without (CC: 0.9 mg kg^{-1}, no CC: 2 mg kg^{-1}; two-way ANOVA, CC $p < 0.001$; Fig. 2A). We found a similar trend at Kirkpatrick (Fig. 2B), but the differences were not statistically significant. Soil NO_3^--N was significantly lower for fields with CC compared to fields with no CC at both Shatto (CC: 2 mg kg^{-1}, no CC: 5 mg kg^{-1}; two-way ANOVA, CC $p < 0.001$; Fig. 2C) and for Kirkpatrick (CC: 3 mg kg^{-1}, no CC: 8 mg kg^{-1}; two-way ANOVA, CC $p = 0.001$; Fig. 2D). There was no effect of cash crop planted during the prior season, or an interaction between prior cash crop and soil DIN, suggesting that CC coverage was effective when planted after corn or soybeans for both Shatto (two-way ANOVA, Cash $p > 0.05$, Int $p > 0.05$; Fig. 2) and Kirkpatrick (two-way ANOVA, Cash $p > 0.05$, Int $p > 0.05$; Fig. 2).

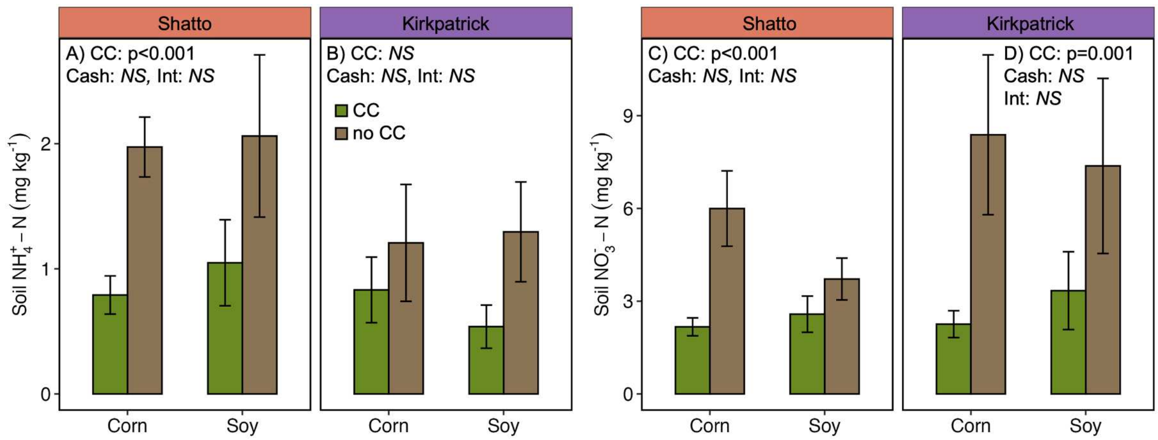

Fig. 2. Comparison of soil NH_4^+-N and NO_3^--N from fields with and without CC according to the cash crop planted during the previous year in each watershed (Shatto: n = 6, Kirkpatrick: n = 3). Differences assessed using two-way ANOVA at α= 0.05. Abbreviation *Int.* represents the interaction of the Cover Crop * Cash Crop main effects.

In fields, soil organic matter (as %) was lower overall at Shatto (3 ± 0.1 %) relative to Kirkpatrick (4 ± 0.2 %; two-way ANOVA Watershed $p < 0.001$). Fields without CC also had higher soil organic matter (3.5 ± 0.2 %) compared to those with CC at both Shatto and Kirkpatrick (2.9 ± 0.1 %; two-way ANOVA CC $p = 0.003$; Fig. 3A). We found no relationship between organic matter (%) and soil DIN, as NH_4^+-N or NO_3^--N (Fig. 3C,E). Cover crop biomass was similar between the watersheds and was not related to soil NH_4^+-N (Fig. 3D), although we observed a marginally significant decrease in soil NO_3^--N with increasing CC biomass (Fig. 3F, $p = 0.07$).

3.2. Effects of cover crops on field-scale on NH_4^+-N and NO_3^--N losses

The effectiveness of CC in reducing NH_4^+-N loss varied over time, and patterns differed for each watershed. At Shatto, annual NH_4^+-N loss from fields with CC ranged from 97 % lower during water year 2022 (Mann-Whitney U, $p < 0.001$; Table 2) to 31 % higher during water year 2017 (Mann-Whitney U, $p < 0.001$; Table 2) compared to tiles with no CC. Median NH_4^+-N loss from tile drains with CC was 1 μg s^{-1} (range=0.002–2261 μg s^{-1}; Fig. 4A), and median NH_4^+-N loss from tile drains without CC was 2 μg s^{-1} (range=0.004–3122 μg s^{-1}; Fig. 4A). At Kirkpatrick, we measured a 75 % increase in NH_4^+-N losses from tile drains with CC compared to drains without CC during water year 2020 (Mann-Whitney U, $p = 0.001$; Fig 4.4B, Table 2), but we did not observe differences between CC drains and no CC drains during other study years. Median NH_4^+-N loss at Kirkpatrick was 2 μg s^{-1} (range=0.003–723 μg s^{-1}) and did not vary between CC and no CC tile drains when data were pooled across study years. Overall, at Shatto, we did not see a difference in the proportion of DIN lost as NH_4^+-N from tile drains. In contrast, at Kirkpatrick, we saw a general increase in NH_4^+-N: DIN ratios with CC, and the proportion measured of NH_4^+-N from tile drains with CC ranged from 35 % to 85 % higher compared to tile drains without CC (data not shown).

Despite comparable soil NH_4^+-N and NO_3^--N pools, annual tile losses for NO_3^--N were 1000x higher than NH_4^+-N when averaged across watersheds and CC status. At Shatto, CC reduced NO_3^--N losses from tile drains by 58–87 % during five of eight study years (Mann-Whitney U, $p \leq 0.007$; Fig. 4C, Table 2). Median NO_3^--N loss from tiles drains with and without CC was 2.1 mg s^{-1} (range=0.007–278 mg s^{-1}) and 4.6 mg s^{-1} (range=0.02–339 mg s^{-1}), respectively. At Kirkpatrick, CC reduced tile NO_3^--N losses during two of eight water years, a 93 % reduction in water year 2022 and a 99 % reduction in water year 2021 (Mann-Whitney U, $p < 0.001$; Fig. 4D, Table 2). We also observed 15 % increase in NO_3^--N losses from CC tile drains compared to no CC drains in water year 2020 (Mann-Whitney U, $p = 0.002$; Fig. 4C, Table 2). Median NO_3^--N loss from tiles drains with CC was 3.0 mg s^{-1} (range=0.006–93.2 mg s^{-1}; Fig. 4D), while median NO_3^--N loss from no CC tiles drains was 3.6 mg s^{-1} (range=0.02–692 mg s^{-1}; Fig. 4D). Based on these median values, CC reduced field-scale NH_4^+-N losses by 45 % (Mann-Whitney U, $p < 0.001$) and NO_3^--N losses by 65 % (Mann-Whitney U, $p < 0.001$; Table 2) when data from both watersheds are pooled.

Seasonality emerged as a strong driver of tile drain NH_4^+-N and NO_3^--N losses but was not as important for soil DIN pools. Tile NH_4^+-N loss in spring was 44 % higher at Shatto (two-way ANOVA Season $p = 0.02$; Fig. 5A, Table 3) and 72 % higher at Kirkpatrick compared to the fall (two-way ANOVA Season $p = 0.02$; Fig. 5C, Table 3). Tile NO_3^--N losses in spring exceeded those in fall by 70 % Shatto (two-way ANOVA Season $p = 0.01$; Fig. 5B, Table 3), or by 38 % when we pooled soils data across the watersheds (two-way ANOVA Season $p = 0.006$; Table 3), but remained consistent between fall and spring samplings at Kirkpatrick. Soil NO_3^--N declined by 50 % between the fall and spring samplings at Shatto (two-way ANOVA Season $p < 0.001$; Fig. 5B, Table 3), or by 38 % when we pooled soils data across the watersheds (two-way ANOVA Season $p < 0.001$; Table 3), but remained consistent between fall and spring samplings at Kirkpatrick. The soil NH_4^+-N pool remained unchanged between fall and spring samplings in both watersheds (Fig. 5A, C, Table 3).

3.3. Watershed DIN export was related to tile drain losses

Overall, DIN concentrations and loads at each watershed outlet were typically related to inputs from tile drains (Fig. 6A-H). For concentrations, we compared each watershed outlet value to the mean for all tile samples collected on the same sampling date (Fig. 6A-D). We found a positive relationship between watershed outlet and tile NH_4^+-N concentrations at Kirkpatrick where 19 % of the variation in the outlet could be explained by tile concentration (R^2=0.19, $p < 0.05$; Fig. 6B), but we found no significant relationship at Shatto (Fig. 6A). In contrast, we found a significant positive relationship between outlet NO_3^--N concentrations and tiles for both watersheds, where tile NO_3^--N concentration explained 16 % of variation at the outlet for Shatto (R^2=0.16, $p < 0.001$; Fig 4.6 C) and 61 % of variation at the outlet for Kirkpatrick (R^2=0.61, $p < 0.001$; Fig. 6D). In addition, for Shatto, we found that most points fell below the 1:1 relationship line, but points measured under higher flow conditions approached the 1:1 line (Fig. 6C). In contrast, for Kirkpatrick, NO_3^--N concentration at the outlet was similar to the mean tile concentration, and consequently, most points fell close to the 1:1 line (Fig. 6D).

Relationships between nutrient load at each outlet and total nutrient loss from all tile drains sampled on a given sampling date (i.e., a rough

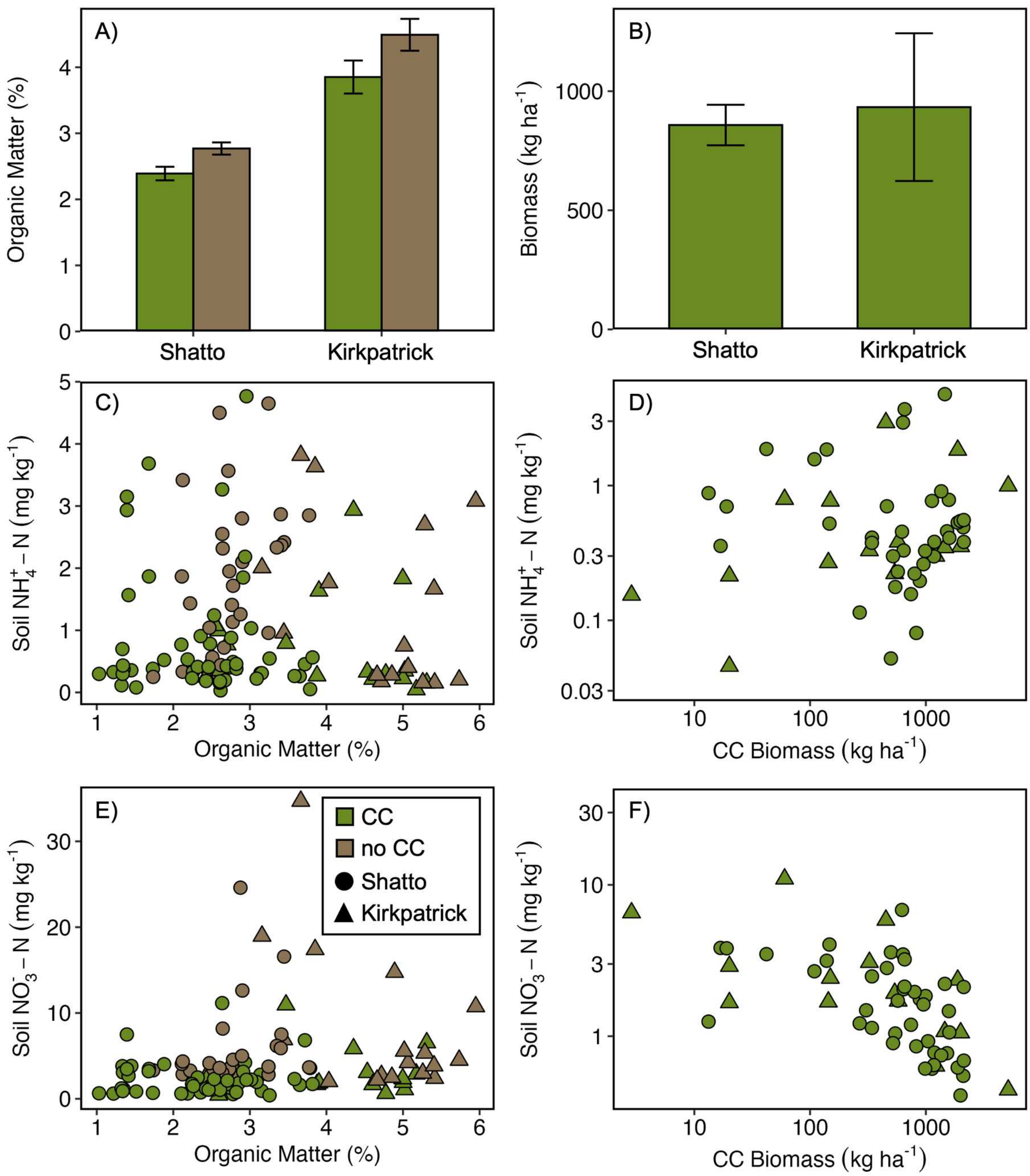

Fig. 3. Comparison of A) soil organic matter (%) and B) CC biomass measured in CC and no CC fields at Shatto (CC: n = 54, no CC: n = 27) and Kirkpatrick (CC: n = 19, no CC: n = 19). Scatter plots compare soil NH_4^+-N or NO_3^--N with organic matter (%; C,E) or CC biomass (D,F).

mass balance) were also significant for both NH_4^+-N and NO_3^--N and at both watersheds; for both forms of DIN, loads at the watershed outlet were typically higher than total tile losses (i.e., most points fell above the 1:1 line; Fig. 6E-H). Total NH_4^+-N losses (kg d^{-1}) from tile drains explained 26 % of the variation in outlet NH_4^+-N loads (kg d^{-1}) at Shatto (R^2=0.26, $p < 0.001$; Fig. 6E) and 18 % at Kirkpatrick (R^2=0.18, $p < 0.001$; Fig. 6F). The explanatory power of total tile losses on outlet loads was higher for NO_3^--N, for which total tile losses explained 62 % of the variation in outlet export at Shatto (R^2=0.62, $p < 0.001$; Fig. 6G) and 40 % at Kirkpatrick (R^2=0.40, $p < 0.001$; Fig. 6H). Finally, NO_3^--N loads diverged according to flow percentile with the highest NO_3^--N loads coinciding with the highest flows (Fig. 6G,H), but this distinction was less clear for NH_4^+-N (Fig. 6E,F).

3.4. Water loss and cover crops control watershed yields

We found that NH_4^+-N and NO_3^--N yields during the fallow season differed among watersheds, where average daily yield of NH_4^+-N was higher at Shatto (0.001 ± 0.00008 kg NH_4^+-N ha^{-1} d^{-1}) than Kirkpatrick (0.0003 ± 0.00003 kg NH_4^+-N ha^{-1} d^{-1}; Mann-Whitney U, $p < 0.001$). In contrast, NO_3^--N daily yield was lower at Shatto (0.07 ± 0.002 kg NO_3^--N ha^{-1} d^{-1}) than at Kirkpatrick (0.1 ± 0.005 kg NO_3^--N ha^{-1} d^{-1}; Mann-Whitney U, $p < 0.001$). Average daily Q (L s^{-1}) varied across water years in both watersheds (Fig. 7A,D). In general, we found that patterns in average NO_3^--N yield followed the pattern established by Q, where years with high flow were strongly associated with high NO_3^--N yield for both watersheds (Kendall τ=0.71–0.87, $p < 0.001$). Watershed-scale NH_4^+-N yields were also driven by Q (Kendall

Table 2
Mean(±SE) losses of NH_4^+-N and NO_3^--N from tile drains underlying fields with and without cc during each study year and over the whole study period. Percent reductions from CC fields compared to no CC fields are calculated for each water year using mean losses. Bolded reductions denote a significant change between CC treatments assessed using Mann-Whitney U Test with a Bonferroni-corrected p-value (Shatto: 0.05/8 = 0.006; Kirkpatrick: 0.5/7 = 0.007).

		NH_4^+-N Loss ($\mu g\ s^{-1}$)			NO_3^--N Loss ($mg\ s^{-1}$)		
	Water Year	**no CC (Mean±SE)**	**CC (Mean±SE)**	**CC Reduction (%)**	**no CC (Mean±SE)**	**CC (Mean ± SE)**	**CC Reduction (%)**
Shatto Ditch Watershed	**2016**	25.2 ± 4.9	2.7 ± 0.5	**−89 %**	17.7 ± 2.8	2.2 ± 0.3	**−87 %**
	2017	20.9 ± 5	30.4 ± 15.4	**(+31 %)**	18 ± 2.9	7.5 ± 1.1	**−58 %**
	2018	24 ± 6.6	26.6 ± 8.5	(+10 %)	14.6 ± 3.6	6.3 ± 1.0	**−57 %**
	2019	*No tiles*	49 ± 18.2	*NA*	*No tiles*	13.1 ± 2.8	*NA*
	2020	30.7 ± 7.5	25.6 ± 9.1	**−17 %**	10.7 ± 1.7	6.9 ± 1.0	−35 %
	2021	28.3 ± 19.7	4.9 ± 2.4	−83 %	8.1 ± 2.0	9.4 ± 3.2	(+14 %)
	2022	51.3 ± 15	1.5 ± 0.3	**−97 %**	14.4 ± 2.7	3.9 ± 0.8	**−73 %**
	2023	40.3 ± 23.1	0.9 ± 0.6	−98 %	6.3 ± 1.1	0.9 ± 0.3	**−85 %**
Kirkpatrick Ditch Watershed	**2016**	9.5 ± 4	18.1 ± 10.8	(+48 %)	15.4 ± 5.9	11.4 ± 2.6	−26 %
	2017	10.8 ± 3.6	10 ± 2.6	−8 %	22.3 ± 6.2	5.9 ± 0.8	−74 %
	2018	51.9 ± 17.8	11.2 ± 2.6	−78 %	12.6 ± 2.9	7.2 ± 0.9	−43 %
	2019	19.4 ± 6.2	14.6 ± 5.4	−25 %	17 ± 5.6	7 ± 1.7	−59 %
	2020	5.6 ± 0.9	22.4 ± 6.2	**(+75 %)**	7.2 ± 1.1	8.5 ± 1.2	**(+15 %)**
	2021	12.8 ± 4.9	1.1 ± 0.3	−92 %	44.2 ± 15.9	0.6 ± 0.2	**−99 %**
	2022	42.5 ± 10.1	2.3 ± 0.3	−95 %	45.9 ± 12.8	3.4 ± 0.6	**−93 %**
	OVERALL	26.7 ± 9.3	14.7 ± 5.5	**−45 %**	18.2 ± 4.8	6.3 ± 1.2	**−65 %**

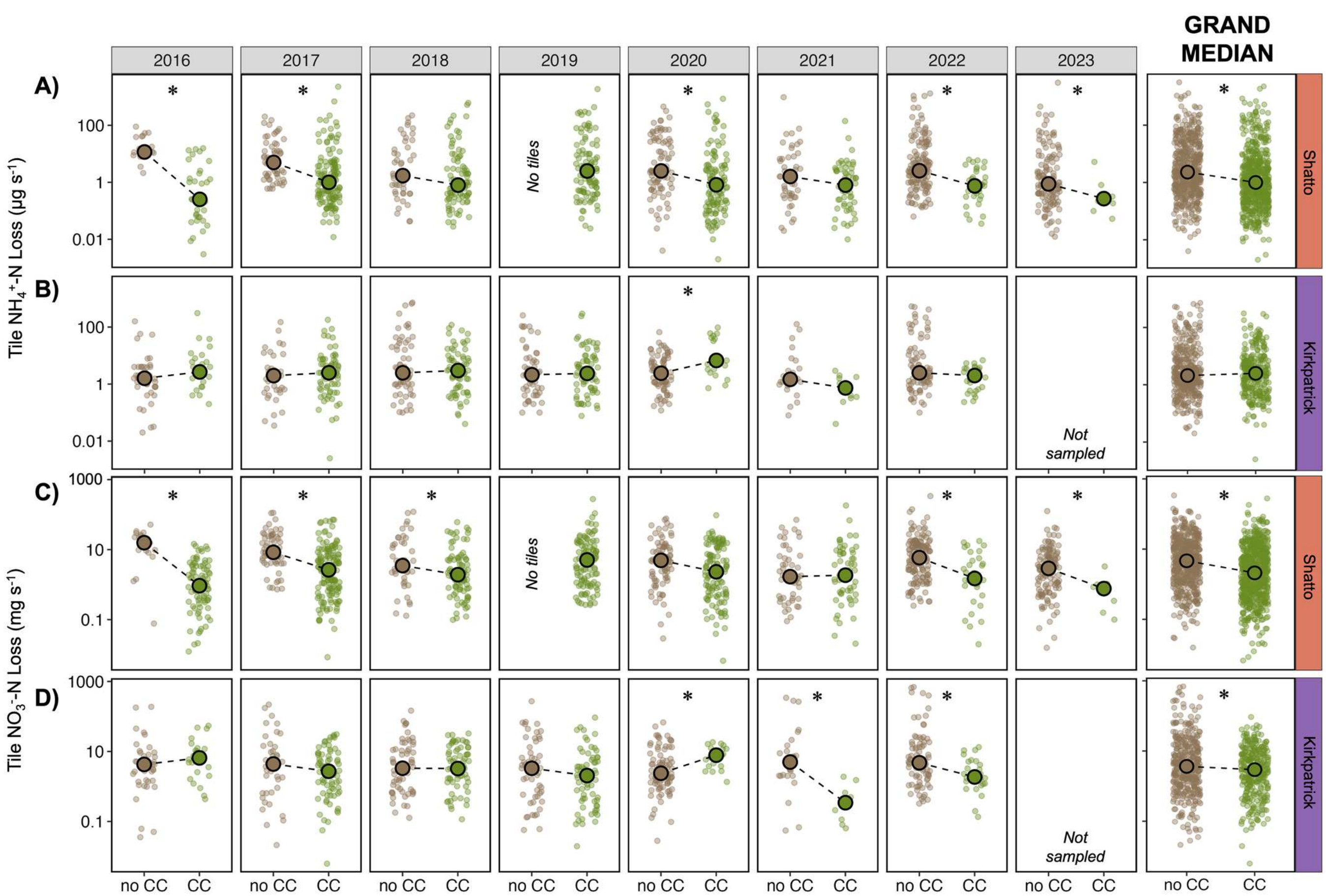

Fig. 4. Comparison of median field-scale losses from tile drains of NH_4^+-N (A,B) and NO_3^--N (C,D) under fields with and without CC during the fallow period at Shatto (A,C) and Kirkpatrick (B,D) for each study year. We pooled study years for each watershed to examine grand NH_4^+-N medians (E,F) and NO_3^--N medians (G,H). Small dots represent instantaneous tile drain loads. Larger dots represent the mean for each treatment. Asterisks denote a significant reduction or increase in nutrient losses from drains with CC relative to those without. There were no tiles draining fields without CC at Shatto during water year 2019, and Kirkpatrick was not sampled during water year 2023. All differences were assessed using a Mann-Whitney U Test with a Bonferroni correction to account for each water year at α= 0.05/7 = 0.007. Grand medians were assessed using a Mann-Whitney U Test at α= 0.05.

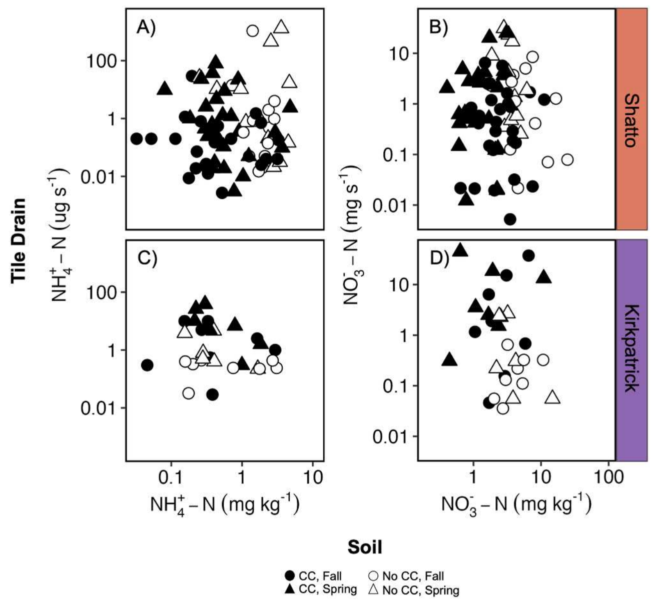

Fig. 5. Comparison of tile drain losses and soil concentrations of NH_4^+-N (A,C) and NO_3^--N (B,D) for Shatto and Kirkpatrick. Each point represents a soil measurement taken in Fall (circles) or Spring (triangles) paired with the corresponding tile drain measurement from the nearest sampling date. Points are colored based on the presence of CC (filled) or lack thereof (open).

Table 3
P value results for two-way ANOVA analysis comparing the effects of CC coverage and season for NH_4^+-N and NO_3^--N measured in soils and tile drains at Shatto and Kirkpatrick. Bolded values indicate a significant result.

	Cover Crop	Season	Cover*Season
Soil NH_4^+-N (mg kg^{-1})			
Shatto	**< 0.001**	0.28	0.52
Kirkpatrick	0.25	0.73	0.34
Shatto+Kirkpatrick	**< 0.001**	0.49	0.26
Soil NO_3^--N (mg kg^{-1})			
Shatto	**< 0.001**	**< 0.001**	0.95
Kirkpatrick	**0.001**	0.23	0.64
Shatto+Kirkpatrick	**< 0.001**	**< 0.001**	0.71
Tile NH_4^+-N (µg s^{-1})			
Shatto	**0.05**	**0.02**	0.92
Kirkpatrick	**0.003**	**0.02**	0.76
Shatto+Kirkpatrick	0.35	**0.006**	0.97
Tile NO_3^--N (mg s^{-1})			
Shatto	**0.04**	**0.01**	0.69
Kirkpatrick	**0.001**	0.11	0.96
Shatto+Kirkpatrick	0.94	**0.006**	0.71

τ=0.58–0.73, p < 0.001), although not as closely (Fig. 7B,E).

We found that while runoff varied among water years, it was relatively consistent between the two watersheds (Fig. 8A,B). Despite this, we observed a mismatch in the magnitude of cumulative NH_4^+-N and NO_3^--N yields between the two watersheds where NH_4^+-N yield was higher at Shatto for most study years compared to Kirkpatrick (Fig. 8C, D), while NO_3^--N yield was higher at Kirkpatrick compared to Shatto (Fig. 8E,F). Cumulative yields of NH_4^+-N and NO_3^--N occurred mainly during the fallow season (Day 1–227 of water year); however, the pattern in increases differed between DIN solutes (Fig. 8C-F). Cumulative NH_4^+-N yields (kg ha^{-1}) followed a step-function pattern over time (Fig. 8C,D) and given the pattern for cumulative runoff (Fig. 9A,B), demonstrated the contribution of event-driven (i.e., storm) export. In contrast, NO_3^--N displayed a constant accumulation over time (Fig. 8E,F) and a linear relationship with runoff (Fig. 9C,D) for both watersheds.

When we pooled fallow season data from Shatto and Kirkpatrick, we found a positive correlation between total runoff and both NH_4^+-N yield (Kendall's τ=0.45, p = 0.02; Fig. 10A) and NO_3^--N yield (Kendall's τ=0.39, p = 0.04; Fig. 10B). When separated by watershed, there was also a marginal association between total runoff and NH_4^+-N yield at Shatto (Kendall's τ=0.57, p = 0.06) and NO_3^--N yield (Kendall's τ=0.71, p = 0.01) at Shatto. In contrast, we did not find these relationships for Kirkpatrick, where land management differs and fields are farther away from the stream edge relative to Shatto. We did not find a significant association between DIN yield and CC coverage in either watershed, or when data were pooled, likely due to higher runoff during the fallow period. However, a lower percent CC coverage at Kirkpatrick (8–32 %) corresponded to overall higher NO_3^--N yields compared to Shatto, where percent CC coverage was higher (21–68 %; *t*-test percent CC p = 0.002) during the study period (Fig. 8B).

4. Discussion

4.1. Soil NH_4^+-N and NO_3^--N dynamics in agricultural fields

The assimilation of soil NH_4^+-N and NO_3^--N into plant or microbial biomass can reduce leachable DIN during the winter and spring fallow season. Reduction of the soil NO_3^--N pool in spring is well-documented in agricultural landscapes (Christopher et al., 2021; Dean and Weil, 2009; Krueger et al., 2011; Kuo and Jellum, 2002). Furthermore, the inverse trend we observed demonstrating a decline in soil NO_3^--N with increasing CC biomass (Fig. 3F) has previously been shown in our watersheds (Christopher et al., 2021) and confirms the broader notion that CC growth can substantially reduce the leachable NO_3^--N pool in soil (Kladivko et al., 2014; Lacey and Armstrong, 2015). In contrast, the lack of seasonality and the poor correlation we observed between soil NH_4^+-N and CC biomass (Fig. 3D; Fig. 5A,C) indicates that NH_4^+-N assimilation into plant biomass is not the sole driver controlling soil NH_4^+-N dynamics in our study system. Soil NH_4^+-N from excess N-fertilizer is susceptible to rapid nitrification (Norton and Ouyang, 2019; Sha et al., 2020) which contributes to the soil NO_3^--N pool and is then susceptible to loss via tile drains which occurs on scales orders of magnitude higher than NH_4^+-N losses, or as runoff (Sebilo et al., 2013; Speir et al., 2022; Tortoso and Hutchinson, 1990) and may be confounded by environmental variability (e.g., precipitation) across the study period. Moreover, biological removal becomes less efficient as pools are depleted (Bender and van der Heijden, 2015). The results of our study are focused on the dynamics between the inorganic NH_4^+-N and NO_3^--N pools in soils and their relationship to tile loss and watershed export.

One component not considered in this study is that of soil organic N, which has been shown to increase significantly with increased CC coverage and concurrent use of modified tillage techniques (e.g., conservation tillage), which we observe in our study watersheds (Blanco-Canqui et al., 2012; Mazzoncini et al., 2011). In agricultural soils, the microbial community is a substantial component of the organic N pool (Gentry et al., 1998; Muhammad et al., 2021). Consistent CC coverage has previously been linked to an increase in the bacterial and fungal community diversity in soils (Brennan and Acosta-Martinez, 2017; Njeru et al., 2015, 2014), and moreover, soil microbes have been shown to preferentially remove NH_4^+-N relative to NO_3^--N in agricultural soils (Gentry et al., 1998; Ma et al., 2021). Compared to the decline in the soil NO_3^--N pool in spring documented here, and shown previously in our study watersheds (Christopher et al., 2021), consistent measurements of soil NH_4^+-N in fall and spring for our CC fields can be explained by the prevalent use of cereal CC species in Shatto and Kirkpatrick. Compared to winter-kill CC species (e.g., oats and radish), cereals continue growing until termination with herbicides or when producers live-plant (seen at Shatto). This continuous living cover spanning the duration of the fallow period prevents changes in the soil NH_4^+-N pool that would otherwise occur through the mineralization of

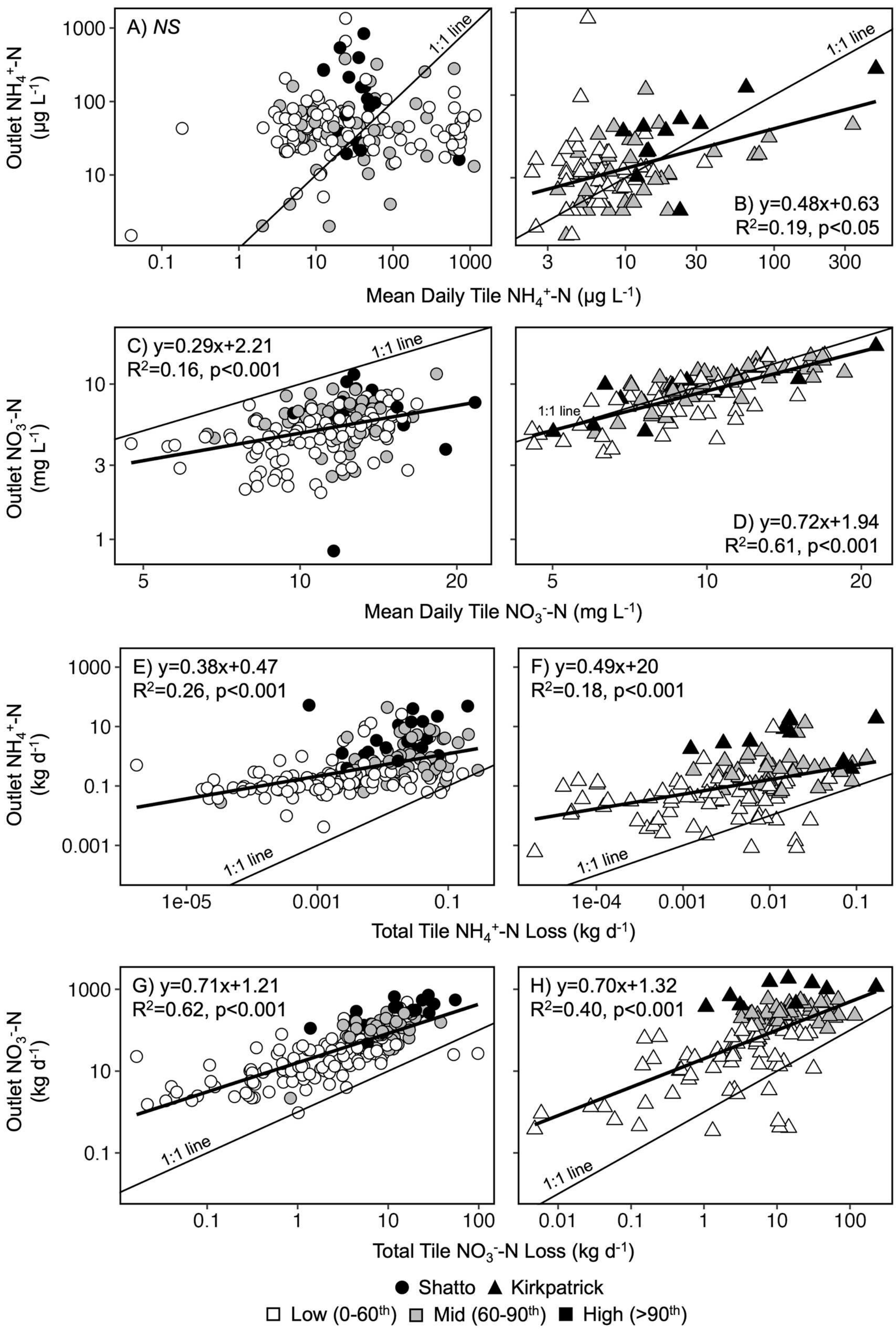

Fig. 6. Relationship between the watershed outlet and the mean for all tile drains on a given sampling date for NH_4^+-N (A,B) and NO_3^--N (C,D) concentrations. Watershed load and total tile loss of NH_4^+-N (E,F) and NO_3^--N (G,H) on a given sampling date. Data are categorized according to flow percentiles assigned using flow duration analysis with lowest flows in white, medium flows in gray, and highest flows in black. A 1:1 line is shown for reference, where points below the line represent dilution of tile inputs at the watershed scale, while points above the 1:1 line suggest additional inputs of N from sources other than tile drains. Dark solid lines represent significant linear regressions.

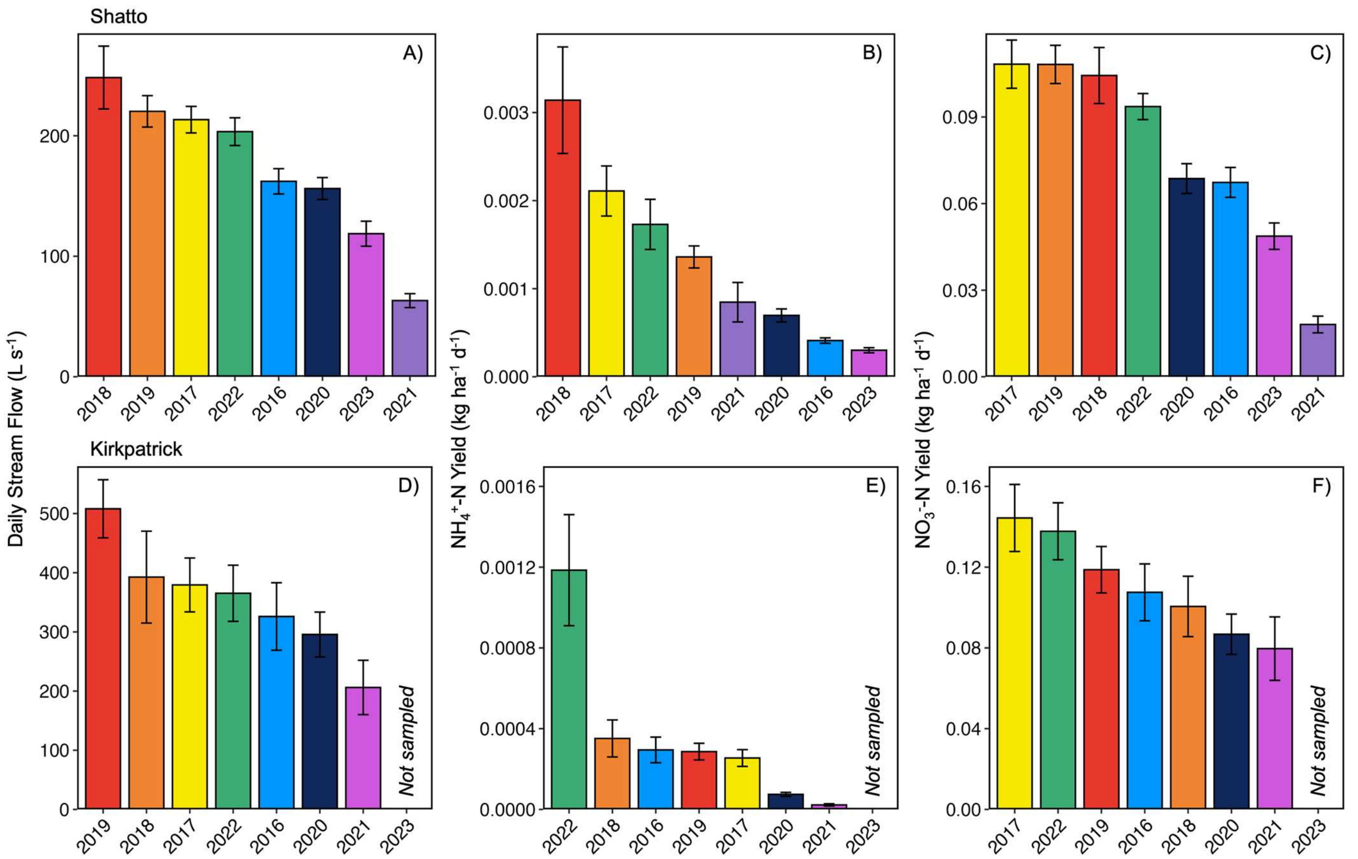

Fig. 7. Mean (± SE) daily stream flow during the fallow season at A) Shatto and D) Kirkpatrick compared to modeled NH_4^+-N (B,E) and NO_3^--N (C,F) daily yields during each water year of the study. Bars are ordered by decreasing magnitude and colored based on flow from highest daily flows (red) to lowest (violet). Colors for each water year are established according to daily stream flow (A,D) and kept consistent for yield panels (B,C,E,F).

plant matter during the wet winter and spring seasons (Duiker, 2014; Rosecrance et al., 2000). In this study, CC effectively reduced the leachable pools of soil NH_4^+-N and NO_3^--N, which has positive implications for water quality in adjacent streams. The disparity we observed in the relationship, or lack thereof, between soil NH_4^+-N or NO_3^--N and CC biomass, combined with seasonal differences observed between the NH_4^+-N and NO_3^--N pools, indicates that different mechanisms control the leachable NH_4^+-N and NO_3^--N pools.

4.2. Cover crops reduce field-scale NH_4^+-N and NO_3^--N, but losses are decoupled

Differences in the mechanisms controlling soil NH_4^+-N and NO_3^--N pools translated to a decoupling of field-scale NH_4^+-N and NO_3^--N losses from tile drains. At the field-scale, we hypothesized that CC would effectively assimilate NH_4^+-N into CC biomass or soil organic N (Christopher et al., 2021; Muhammad et al., 2021), thus reducing edge-of-field NH_4^+-N losses and altering DIN stoichiometry from tile drains compared to fields left fallow after harvest. Similar to other studies, tile drain NH_4^+-N losses at Shatto and Kirkpatrick from fields with and without CC occurred on a much lower scale compared to NO_3^--N losses measured at the same time (Drury et al., 1993; Gentry et al., 1998). The effect of CC on field-scale NH_4^+-N losses was not as consistent as the patterns previously documented for NO_3^--N in our watersheds which has been linked to patterns in runoff and tile Q (Hanrahan et al., 2018; Speir et al., 2022). This points to different drivers of NH_4^+-N loss compared to NO_3^--N and suggests that tile flow likely plays a smaller role in driving edge-of-field NH_4^+-N loss. Given we observed comparable soil NH_4^+-N pools at Shatto and Kirkpatrick, the 35–85 % increase we observed in the proportion of DIN lost as NH_4^+-N at Kirkpatrick, and no change observed at Shatto, can be attributed back to the general soil characteristics at this site including higher organic matter (Fig. 3A). The combination of warmer temperatures and accelerated snowmelt events, which are expected to coincide with climate change in Indiana (Hamlet et al., 2020; Widhalm et al., 2018), have been shown to enhance rates of organic matter decomposition and subsequent NH_4^+-N mineralization (Yang, 2006), and thus, may help to explain fewer years with significant NH_4^+-N reductions with CC coverage, and more frequent increases compared to NO_3^--N. Furthermore, as temperatures warm and snow cover decreases, routine freezing and thawing of soils may exacerbate the lysis of microbial and plant root cells (Henry, 2007), and increase the leachable NH_4^+-N pool (Blankinship and Hart, 2012; Elliott and Henry, 2009). Despite interannual variability, and differences between the watersheds, we note that the conservation signature of planting CC still resulted in a significant 45 % reduction in NH_4^+-N losses from tile drains when data from both watersheds and across all study years are pooled (Table 2).

Cover crops had a more consistent and positive effect on tile drain NO_3^--N losses during the study period. While the magnitude of CC effects on NO_3^--N losses varied among years and between the two watersheds (Table 2), our results show that CC can reduce field-scale NO_3^--N losses by 65 % when study years from both watersheds are pooled (Mann-Whitney U, $p < 0.001$; Table 2). This result aligns with prior work completed in the systems (Hanrahan et al., 2018; Speir et al., 2022) and confirms the efficacy of CC as a strategy to mitigate NO_3^--N loss from tile drains in the midwestern Corn Belt (Hanrahan et al., 2021; Jaynes et al., 2001; Kladivko et al., 1991). Given the leaky nature of NO_3^--N, increased NO_3^--N losses are frequently attributed to concurrent increases in tile flow (Cuadra and Vidon, 2011; Hanrahan et al., 2018). Similar to past results (Speir et al., 2022), reduced NO_3^--N losses from CC tile drains

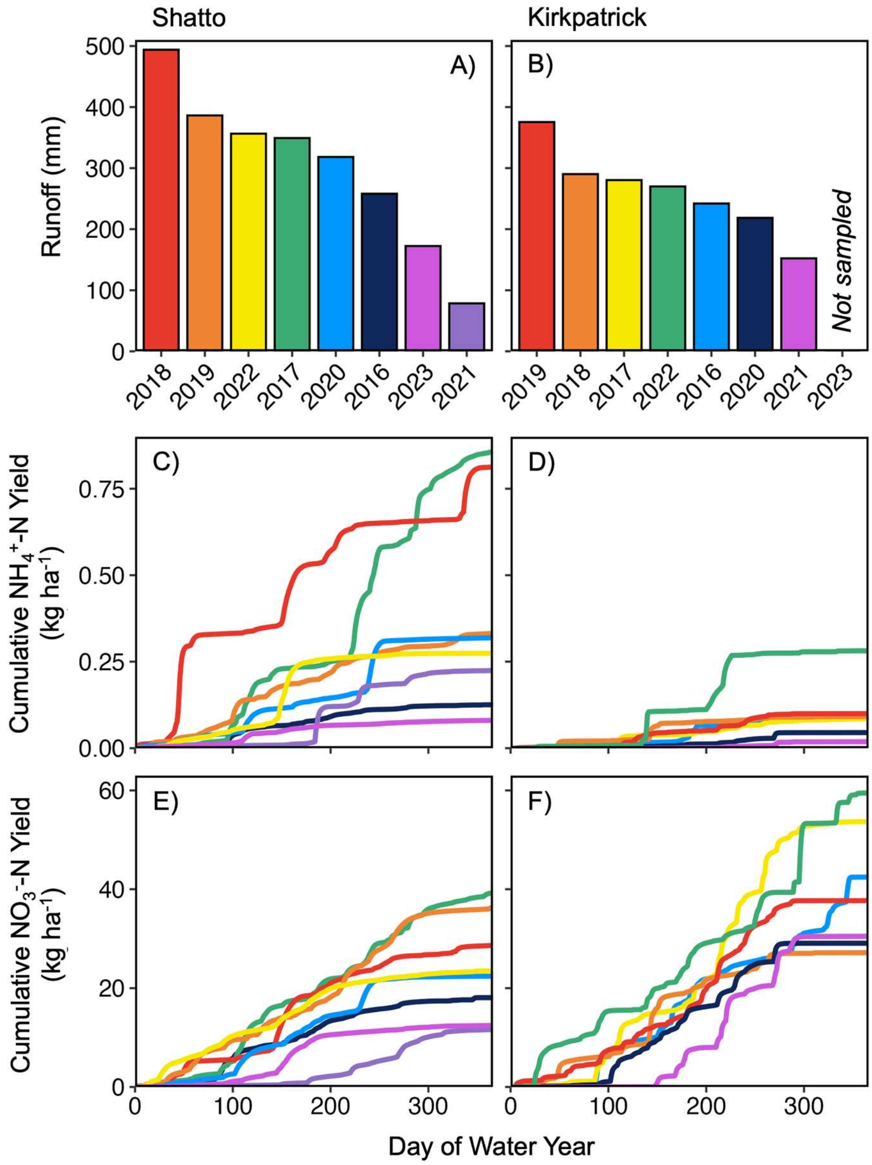

Fig. 8. Annual runoff for each water year at Shatto (A; left column) and Kirkpatrick (B; right column) included in the study. Cumulative NH_4^+-N (C,D) and NO_3^--N (E, F) yield plotted against day of the water year (October 1 through September 30) to examine the timing of nutrient yields and the role of event-driven losses (i.e., storms). Color palette for cumulative losses at Shatto (left) is defined in panel A, and palette for Kirkpatrick (right) is defined in panel B.

mirrored reductions in tile flow in this study (data not shown). Differences in the NO_3^--N loss patterns observed between Shatto and Kirkpatrick can be partially attributed to CC species assemblage and overall coverage, as well as organic matter content (Christopher et al., 2021). Another study has shown that over-wintering CC species, including cereal rye, reduced NO_3^--N leaching by stabilizing DIN in the soil profile relative to winter-kill species (Lacey and Armstrong, 2015). We observed greater use of cereal and annual ryegrass species (data not shown) and overall higher CC coverage at Shatto (Table 1), while Kirkpatrick had more instances of winter-kill CC (e.g., oats and radish) which could have resulted in more rapid mineralization during the late winter and spring, changes to the soil NO_3^--N pool, and increases in NO_3^--N loss from tile drains. Despite being in the same region, these two watersheds present different environmental settings which include underlying soil chemistry and land management regimes; this context, combined with the positive effects of CC documented here, ultimately demonstrate that CC are a robust conservation strategy that can effectively reduce field-scale NO_3^--N losses, and moreover, is an approach that can be adapted across a wide range of agricultural settings.

4.3. *Watershed-scale NH_4^+-N and NO_3^--N export are decoupled but linked by storms*

The signature of DIN export from agricultural watersheds is representative of the collective biogeochemical processes occurring upstream, and has ramifications for downstream water quality (Turner and Rabalais, 1991). Pools of NH_4^+-N and NO_3^--N in surface waters are intrinsically linked via the microbially-mediated process of nitrification in streams (Arango and Tank, 2008; Kemp and Dodds, 2002). However, nitrification in agriculturally dominated headwaters contributes minimally to watershed-scale NO_3^--N export due to elevated NO_3^--N inputs from the surrounding landscape. Despite the overwhelming signature of NO_3^--N on total DIN export from agricultural streams, understanding the timing and patterns of watershed-scale NH_4^+-N export elucidates a component of NH_4^+-N cycling that was not well described until now. At both the tile-drain and watershed scale, we predicted that increased CC coverage in our two study watersheds would result in lower NH_4^+-N losses during the fallow season, and that the magnitude of NH_4^+-N export would be much lower compared to NO_3^--N due to preferential NH_4^+-N

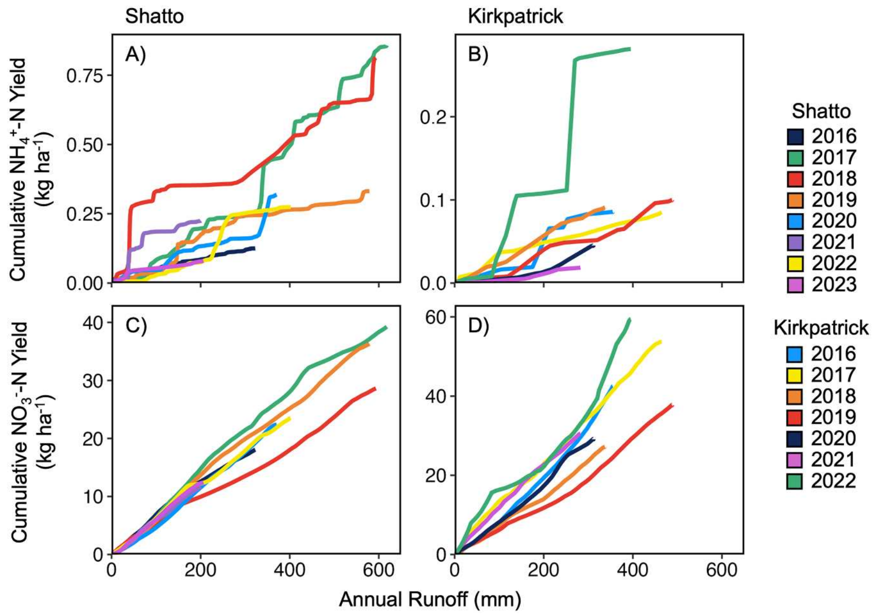

Fig. 9. Cumulative NH_4^+-N (A,B) and NO_3^--N (C,D) yield plotted with cumulative runoff to examine the effect of water loss on nutrient yields.

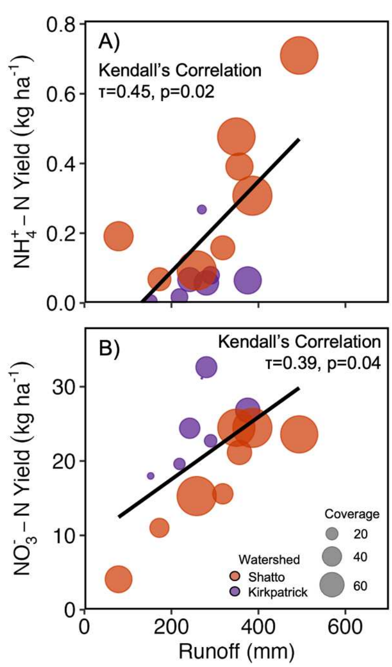

Fig. 10. Assessment of the relationship between total A) NH_4^+-N and B) NO_3^--N yield and runoff during the fallow season of each water. Points are colored by watershed, and point size corresponds to percent CC coverage for a given year. We include a Kendall correlation to assess association between N yields and runoff.

removal by aquatic biota and tight biogeochemical cycling of NH_4^+-N between organic and inorganic forms (Mulholland et al., 2008; Tank and Dodds, 2003). Finally, we predicted that the timing of NH_4^+-N and NO_3^--N export would mirror one another and be linked to high flow conditions (i.e., storms) when increased flows mobilize NO_3^--N and NH_4^+-N adsorbed to soils or stream sediments (Chen et al., 2018; Royer et al., 2006).

The role of tile losses on watershed-scale dynamics differed between solutes and watersheds. For both watersheds, tile drains could show either a concentrating or diluting effect on NH_4^+-N dynamics compared to the outlets, and a lack of separation in the data by flow percentiles suggests that these dynamics are unrelated to flow during the study period (Fig. 6A,B). For NO_3^--N, we saw a strong signal of NO_3^--N dilution entering the stream from tile drains at Shatto that appeared to dissipate during high flows (Fig. 6C). This signature can be jointly explained by the infiltration of high-NH_4^+-N and low-NO_3^--N groundwater that occurs during low flow conditions (Grose et al., 2022) and the increase in total flow coming from tile drains after storm events, but we note that this groundwater signature is absent at Kirkpatrick. Furthermore, the convergence of tile drain and stream concentrations under high flows at Shatto (Fig. 6C), which also occur consistently at Kirkpatrick (Fig. 6D), may suggest that the ability of these systems to process NO_3^--N diminishes and the streams begin to behave more like throughput systems where little NO_3^--N entering through tile drains is being processed by stream biota (e.g., denitrifying bacteria; Speir et al., 2020). Total nutrient loads consistently fell above the 1:1 line for both NH_4^+-N and NO_3^--N (Fig. 6E-H) which definitively demonstrates that sources in addition to tile outputs contribute to watershed export. The clear separation of points from each flow percentile for NO_3^--N loads (Fig. 6G,H), which is easily transported in surface water and tile drain runoff, is diminished for NH_4^+-N (Fig. 6E,F). These patterns lead us to the conclusion that NH_4^+-N dynamics are not as explicitly linked to water under most flow conditions.

Storms emerged as a critical period of watershed-scale NH_4^+-N and NO_3^--N export. Cumulative NH_4^+-N yields are characterized by strong, episodic step increases which accentuate the role of high-flow events (i.e., storms) as "hot moments" of NH_4^+-N export (Fig. 9A,B), as well as that of other dissolved solutes (NO_3^--N and SRP; Royer et al., 2006; Speir et al., 2021). This pattern strongly contrasts with the gradual increases observed for NO_3^--N (Fig. 9C,D) where the strong correlation between NO_3^--N yield and runoff highlights the role of rainfall and subsequent hydrologic changes (e.g., increased streamflow) as dominant drivers of NO_3^--N losses from agricultural systems (Gorski and Zimmer, 2021; Seybold et al., 2019). Collectively, these results demonstrate that NH_4^+-N is not as susceptible to minor shifts in hydrology. With respect to CC coverage, we did not see a decrease in watershed-scale NH_4^+-N and NO_3^--N yield with increased CC coverage at either Shatto or Kirkpatrick, likely due to higher runoff during the CC period which encompasses the wet winter and spring seasons (Speir et al., 2022). We do note that years with high NH_4^+-N and NO_3^--N yields (and runoff) did coincide with high CC coverage (Fig. 10) which may have mitigated the potential for even higher losses by controlling water holding capacity (Basche and

DeLonge, 2019).

Despite close geographic proximity, we found that differences in the soil setting, stream sediments, and hydrologic conditions result in contrasting patterns in the timing and magnitude of NH_4^+-N and NO_3^--N loss dynamics at the watershed-scale. For instance, NH_4^+-N binds readily to organic matter and clay particles (Sawyer, 2019), both of which are more abundant at Kirkpatrick (Christopher et al., 2021; Trentman et al., 2020) which may help to explain lower NH_4^+-N yields at this site relative to Shatto. Furthermore, groundwater infiltration is a substantial source of NH_4^+-N that is known to vary throughout the year at Shatto (Grose et al., 2022). For NO_3^--N, tile losses occur on the same scale between the two watersheds, but average Q at the outlet is nearly double at Kirkpatrick compared to Shatto (Fig. 4C,D; Fig. 7). In addition, stream sediments at Shatto are rich in fine benthic organic matter, which can enhance microbial activity, including denitrification (Speir et al., 2020). As such, the results of this study demonstrate that environmental context, which includes influences from soil conditions, groundwater dynamics, flow, and CC dynamics, plays a critical role in influencing watershed-scale export patterns for NH_4^+-N and NO_3^--N.

Overall, the results of this study suggest that CC can be used to reduce soil NH_4^+-N and NO_3^--N pools, and field-scale DIN losses, however their efficacy for NH_4^+-N was less consistent on an annual basis, possibly due to variables that can decouple NH_4^+-N and NO_3^--N losses such as the role of streamflow, microbial processing (e.g., assimilation or nitrification), soil chemistry, and environmental variability. Yet, despite the increased variability in NH_4^+-N losses we documented over time, NH_4^+-N was consistently orders of magnitude lower than NO_3^--N for tile- and watershed-scale losses and suggests that soil nitrification has the potential to impact the scale of NH_4^+-N and NO_3^--N losses from tile drains which then cascades to watershed-scale losses. Despite the biogeochemical coupling of NH_4^+-N and NO_3^--N, the strong episodic pattern seen in cumulative NH_4^+-N yields diverged from the more constant increase in NO_3^--N yields, pointing to storms as particularly important periods for managing NH_4^+-N losses from fields. Furthermore, the differences in the magnitude of NH_4^+-N and NO_3^--N losses between Shatto and Kirkpatrick, two watersheds located geographically close to one another, suggests that environmental context (i.e., seasonality, hydrology, and land management) is critical to consider to effectively manage N dynamics in agroecosystems. The management of NH_4^+-N specifically can be achieved via the application of N stabilizers alongside fertilizers (Beeckman et al., 2018; Liu et al., 2022; Sha et al., 2020; Trenkel, 2010), but their use results in added costs for producers. As crop production across the midwestern landscape adapts to climate change and fluctuating environmental conditions, the results of this study demonstrate how the application of cover crops over a multi-year period can mitigate NH_4^+-N losses. Combining cover crops with additional practices, such as the use of N stabilizers, can continue to support high productivity of working lands, prevent unintended losses of N fertilizers, and ensure improved water quality for adjacent waterways and downstream ecosystems.

CRediT authorship contribution statement

Vincent Anna E.S.: Writing – review & editing, Writing – original draft, Visualization, Methodology, Formal analysis, Data curation. **Mahl Ursula H.:** Writing – review & editing, Validation, Project administration, Methodology, Formal analysis, Data curation. **Sethna Lienne R.:** Writing – review & editing, Methodology, Formal analysis. **Rasnake Lindsey M.:** Writing – review & editing, Methodology, Formal analysis. **Royer Todd V.:** Writing – review & editing, Visualization, Validation, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis. **Tank Jennifer L.:** Writing – review & editing, Visualization, Validation, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization. **Pruitt Abagael N.:** Writing – review & editing, Visualization, Methodology, Formal analysis, Data curation. **Speir Shannon L.:** Writing – review & editing, Visualization, Methodology, Formal analysis, Data curation.

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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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.agee.2025.109531.

Data availability

Data will be made available on request.

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