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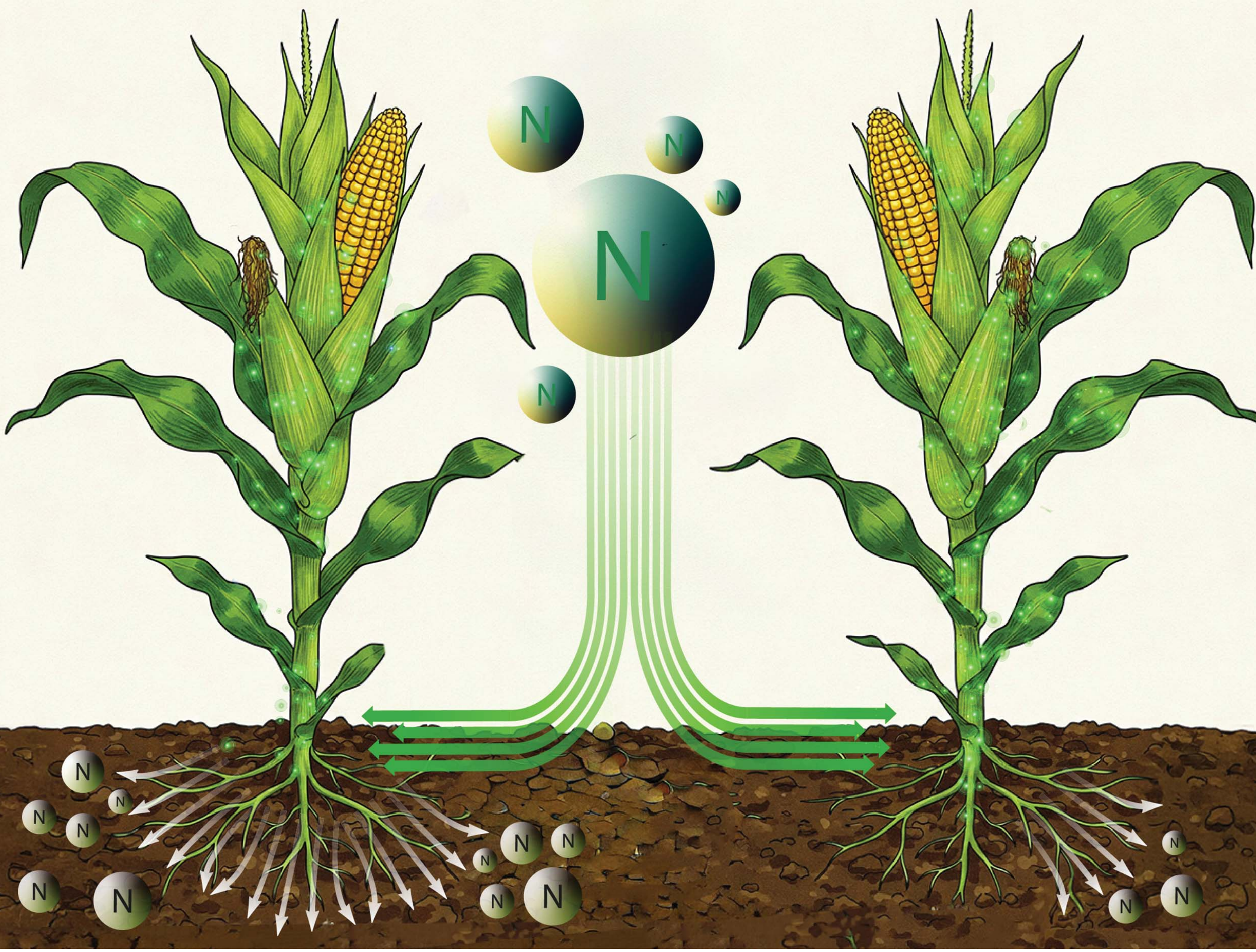

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A mechanistic model for determining factors that influence inorganic nitrogen fate in corn cultivation†

Patrick J. Dunn[a] and Leanne M. Gilbertson *[abc]

Conventional practices for inorganic nitrogen fertilizer are highly inefficient leading to excess nitrogen in the environment. Excess environmental nitrogen induces ecological (*e.g.*, hypoxia, eutrophication) and public health (*e.g.*, nitrate contaminated drinking water) consequences, motivating adoption of management strategies to improve fertilizer use efficiency. Yet, how to limit the environmental impacts from inorganic nitrogen fertilizer while maintaining crop yields is a persistent challenge. The lack of empirical data on the fate and transport of nitrogen in an agriculture soil-crop system and how transport changes under varying conditions limits our ability to address this challenge. To this end, we developed a mechanistic model to assess how various parameters within a soil-crop system affect where nitrogen goes and inform how we can perturb the system to improve crop nitrogen content while reducing nitrogen emissions to the environment. The model evaluates nitrogen transport and distribution in the soil-corn plant system on a conventional Iowa corn farm. Simulations determine the amount of applied nitrogen fertilizer acquired by the crop root system, leached to groundwater, lost to tile drainage, and denitrified. Through scenario modeling, it was found that reducing application rates from 200 kg ha^{-1} to 160 kg ha^{-1} had limited impact on plant nitrogen content, while decreasing wasted nitrogen fertilizer by 25%. Delayed application until June significantly increased the f-NUE and denitrification while reducing the amount of fertilizer leached and exported through tile drainage. The value in a model like the one presented herein, is the ability to perturb the system through manipulation of variables representative of a specific scenario of interest to inform how one can improve crop-based nitrogen management.

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Environmental significance

Inorganic nitrogen fertilization practices in agriculture crop production are linked to downstream environmental impacts such as ecological damage, contaminated drinking water, and greenhouse gas emissions. Developing effective interventions to address these challenges requires first appreciating how the current management practices influence nitrogen fate and transport. Using our developed mechanistic model, we investigate how current practices and natural system parameters (*e.g.*, climate variables) influence partitioning (*i.e.*, plant, leachate, tile drainage, atmospheric emissions) of inorganic nitrogen fertilizer inputs to environmental compartments (soil, air, water). The results are applicable to on-farm activities and can be used to inform modified practices and development of new interventions for improved inorganic nitrogen fertilizer efficacy.

1 Introduction

Technological advancements over the last century enabled an increase in food production. One of the most impactful is the Haber–Bosch in 1913 for the production of inorganic nitrogen fertilizers,[1] which introduced access to affordable, external sources of nitrogen.[2] Nitrogen is a necessary nutrient for crop development and accounts for roughly 59% of all macronutrients applied to crops in the U.S.[3] The current inorganic nitrogen application rate in the U.S. is 11.8 Tg year^{-1}, which is a nearly 4-fold increase since 1960.[3] Fertilizer nitrogen use efficiency (f-NUE), when defined as the ratio of nitrogen fertilizer recovered by a crop to the nitrogen applied as fertilizer, is generally considered to be less than 0.5, meaning a minimum of 50% of applied nitrogen is lost to the environment.[4–6] The massive inputs of inorganic nitrogen fertilizer along with poor f-NUE have caused an imbalance in the nitrogen cycle, which contributes substantial nitrogen emissions to the environment leading to vast downstream environmental impacts, such as

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60% of coastal rivers and bays in the U.S. designated as having moderate to severe ecological damage.[7] Biochemical processes in soil convert different forms of nitrogen to nitrate, which is highly soluble in water, leading to rapid leaching to water bodies.[8] Accumulation of nitrate in groundwater, the drinking water source for 50% of the U.S. population, elevates the risks of cancer and birth defects.[5–7,9]

In addition, large loads of mineral nitrogen are exported from fields to surface waters through tile drainage.[10,11] Cropland in the U.S. is extensively tile drained, with a total of 53 million acres employing tile drainage across the country.[12] Inefficient fertilization also leads to denitrification in soils producing nitrous oxide, a potent greenhouse gas. U.S. cropland contributes 161.6 million megatons of CO_2 equivalents of nitrous oxide annually, which has been linked to the mineral nitrogen surplus in soils emerging from agricultural activity.[13] From an economic perspective, the downstream consequences of excess nitrogen in the environment have an estimated $210B annual impact on the environment and public health in the U.S.[14] The magnitude of agriculture-induced nitrogen cycle imbalance and urgent need for solutions to address low f-NUE has been recognized by the National Academy of Sciences and United Nations as a major engineering challenge of the 21st century.[15,16]

Substantial research has been conducted to develop effective interventions for improving nitrogen fertilizer use in agriculture.[17–19] The goal of these practices and engineered solutions is to deliver nitrogen more effectively and efficiently to meet crop physiological needs while reducing excess nitrogen in the environment. Increasing efficiency has the added benefit of reducing the amount of nitrogen application required for crop production. While best management practices (*e.g.* soil testing, nitrogen budgeting, side-dressing) are well established, newer interventions have emerged including those from the 'regenerative' agriculture movement[20,21] and engineered solutions, such as precision agriculture technologies[22] and slow, controlled, and stimuli responsive release nitrogen fertilizers.[23–32] Regardless of the approach, established or emerging, there is an urgent need to address the unbalanced, crop production-associated nitrogen cycle and there remains a dearth of approaches to offer guidance for a given scenario (*i.e.*, soil characteristics, climate, intervention options).

Developing an effective intervention to rebalance the crop-based nitrogen cycle is difficult due to the array of variables that influence nitrogen fate and transport in soil systems and recovery by crops. These include soil properties (*e.g.*, water retention, porosity, cation exchange capacity, pH, microbial activity), climate variables (*e.g.*, precipitation, temperature), crop root architecture (*e.g.*, root dimensions and spatial density), variable crop developmental demands (*e.g.*, the V6 to VT stages account for 60% of nitrogen uptake in corn),[33] and on-farm practices (*e.g.*, timing and amount of nutrient application). The number and variability in each of these parameters makes identifying the most effective interventions to improve nitrogen management challenging, and empirically testing a new intervention across these numerous variables is incredibly time and resource intensive. Furthermore, continuous measurement of nitrogen dynamics across all nitrogen forms within a crop-soil system is difficult, due to the need for sub-surface remote sensing of nitrogen that is minimally-invasive to the crop.[34] Thus, *in situ* measurement of the spatial dynamics of root growth, nitrogen transport, transformation, and recovery across these variables at a high resolution is not currently possible.[35] Given these challenges and limitations, there is value in the ability to model nitrogen fate, transport, and uptake in a soil-crop system to enable assessment of performance across nitrogen management scenarios.

There are several existing computational tools for assessing biogeochemical nutrient cycling. These tools include large scale models such as The Soil and Water Assessment Tool (SWAT)[36] and DAYCENT,[37] and small-scale models such as RootBox[38] and SimRoot.[39] The large-scale tools are useful for modeling nutrient cycling on the watershed or regional scale; however, these models simplify processes and lack the granularity needed to understand spatiotemporal dynamics related to inorganic nitrogen fertilizer fate and transport. On the other hand, small-scale models (functioning at the cm scale, or smaller) that simulate root architecture and development capture the desired resolution to tackle this study. Yet to date, these models have not been used in conjunction with soil and nutrient transport models to extensively investigate nitrogen transport and plant uptake dynamics.

To this end, we developed a field-scale mechanistic model that captures the transport, biological transformation, and uptake of nitrogen in a soil-crop system that includes a dynamic root system. The model determines the fate of nitrogen in four fate pools, which include the nitrogen recovered by the crop, nitrogen denitrified to gaseous forms, nitrogen leached below the root zone, and nitrogen exported through tile drainage. We applied this model to a study site in Iowa, which was perennially utilized for corn cultivation. Corn was chosen because of its high nitrogen demand (*i.e.*, 50% of all applied inorganic nitrogen fertilizer is used to produce corn)[3] and production volume (15 billion bushels annually in the U.S.).[40] This scenario includes information specific to the location (*i.e.*, soil characteristics and historical daily weather data) over the course of ten study years and was used to assess baseline nitrogen fate and performance (*i.e.*, f-NUE) at the site. In addition, we conducted scenario modeling to evaluate the influence of several different management practices on nitrogen fate and demonstrate the utility of the model to offer insights and guide decision making to those interested in applying the model to their situation. We used results from the different model perturbations to discuss potential implications for implementing and designing interventions for improved nitrogen management in corn cultivation.

2 Methods

2.1 Study site description

The evaluation and application of our model to relevant scenarios for corn cultivation required a data set that includes corn crop management, agronomy, weather, and nitrogen fate in a crop field setting. Such data is needed for inputs to run the model and is used for calibration and validation of the model. To meet this end, we used the Iowa State University Southeast Research and Demonstration Farm study site located in Washington County, Iowa.

The site is a 273 acre farm on flat or slightly sloping land that has been in operation since 1987, growing corn, soybean, and other small grains.[41] Recently, the site was used for the USDA Transforming Drainage Project,[42–44] a research project aimed at evaluating and improving agricultural tile drainage. For the Transforming Drainage project, the study site was split into eight study plots, which were used for corn cultivation each year over the ten study years. In each of these plots, different agricultural drainage systems were studied. For the purposes of the work detailed herein, data were used from two of these study plots, which were conventionally drained through free tile drainage, and each had an area of 1.4 hectares. The other study plots had drainage management practices not relevant to this study, and therefore, their data were not used. Data were used from a 10 year period (2008 to 2017). In each of these years, the two study plots used herein were managed identically. The dominant soil series at this site include the Taintor, Kalona, and Mahaska series, which are all silty clay loams and poorly drained.[42] The site is characterized as having a humid continental climate.[45] Over the ten study years, the site had a mean high temperature of 16 ± 13 °C. Mean annual precipitation at the study site was 850 ± 120 mm over the study period.[42]

Through the USDA Transforming Drainage Project, management practices such as planting dates, nitrogen fertilizer dates, fertilization types and application methods were tracked over the study period. Agronomic data, such as yield, and total plant nitrogen were also collected at time of harvest. Soil chemistry data were listed for the study plots. In addition, daily weather, growing degree days (GDDs), soil moisture, and soil temperature data were collected at the site. Finally, the site monitored daily flows of drainage water and nitrate loads. Data used in this study are publicly available (**https://datateam.agron.iastate.edu/td/dl/#tab_wxdata**).

When necessary data were missing, such as total plant nitrogen and daily soil temperature, well-validated statistical or machine learning prediction models were created to predict these values with high accuracy. Full details and validation of these predictions can be found in the ESI (Fig. S1 and S2†)

The soil system was modeled using the USDA Soil Survey Geographic Database (SSURGO) data for the study site coordinates.[46] The SSURGO map unit for the site was determined. A map unit is a delineated area that is predominantly composed of one soil series. Each map unit is composed of several distinct soil components, which are phases of the soil series. These components each have distinct soil properties listed by depth. To determine the soil properties for our model (*i.e.*, soil hydraulic properties and organic matter composition), the weighted average by depth across the components was calculated. The total depth of the soil system was determined to be 160 cm, which is the average depth of the soil components at the study site.

A variety of fertilizer practices were employed during the study period, including different planting dates, fertilizer application dates, nitrogen fertilizer types, and application methods. Nitrogen fertilizer application amounts ranged from 84 kg ha^{-1} to 220 kg ha^{-1} with a mean application rate of 167 kg ha^{-1}. In eight of the ten years, the main application was anhydrous ammonium injected at a depth of 20 cm. In two of these years, 2010 and 2015, urea ammonium nitrate (UAN) was broadcast following the main application of anhydrous ammonium. In the final two study years, 2016 and 2017, UAN was used as the main fertilizer and was broadcasted to the soil surface. Main fertilizer application dates ranged from April 1st to June 8th. Planting date ranged from April 18th to May 17th over the ten study years.

2.2 Description of model structure

The model developed and applied herein is a mechanistic model that endeavors to combine existing models and theory to capture the fate and transport of nitrogen added to soil for conventional corn cultivation on the field scale. To this end, the model simulates the physical, chemical, and biological processes underlying nitrogen fate and transport in the subsurface given a certain set of input parameters (Fig. 1). Model inputs include daily weather (*i.e.*, precipitation and growing degree days), soil physical and hydraulic properties, daily temperature data, planting date, root system extent by depth, and nitrogen fertilizer management practices. These inputs then control sub-processes such as soil water transport, tile drainage, mineral nitrogen transport, crop nitrogen demands, and biogenic nitrogen transformations. Nitrogen in the system was modeled as four forms: ammonium, nitrate, organic nitrogen, and denitrified (*e.g.*, gaseous). Nitrogen is either background, such as the organic nitrogen and background mineral forms in the soil, or from fertilizer, which was modeled as ammonium. Biogenic mineralization/immobilization, nitrification, and denitrification allowed for transformation and cycling of nitrogen between these different forms. The model does not delineate between these different denitrification products as scientific investigation of the influence of these various factors is still ongoing. Nitrogen coming out of the modeled system entered one of four fate pools: plant nitrogen, tile drainage, denitrified, or leachate. Plant nitrogen is the nitrogen in the system that is acquired by the crop root system. Tile drainage is nitrate that exits the system with water through the tile drain. Denitrified nitrogen is formed from denitrification of soil nitrate, and can form multiple products including diatomic nitrogen, nitric oxide, and nitrous oxide. The portion of denitrified nitrogen that forms nitrous oxide, a potent greenhouse gas, is dependent on various factors such as soil pH, soil texture, oxygen availability, and the presence of certain microbial communities.[47–50] While the model tracks the system nitrogen through denitrification, it does not determine the speciation of denitrification products. Leachate is defined as mineral nitrogen that had leached to depths below 1 meter, where corn roots are unlikely to retrieve it.[51]

The model operates on the hourly timescale and centimeter length scale, and all elements are modeled in one-dimensional spatial scale (*i.e.*, by subsurface depth). Thus, all elements are

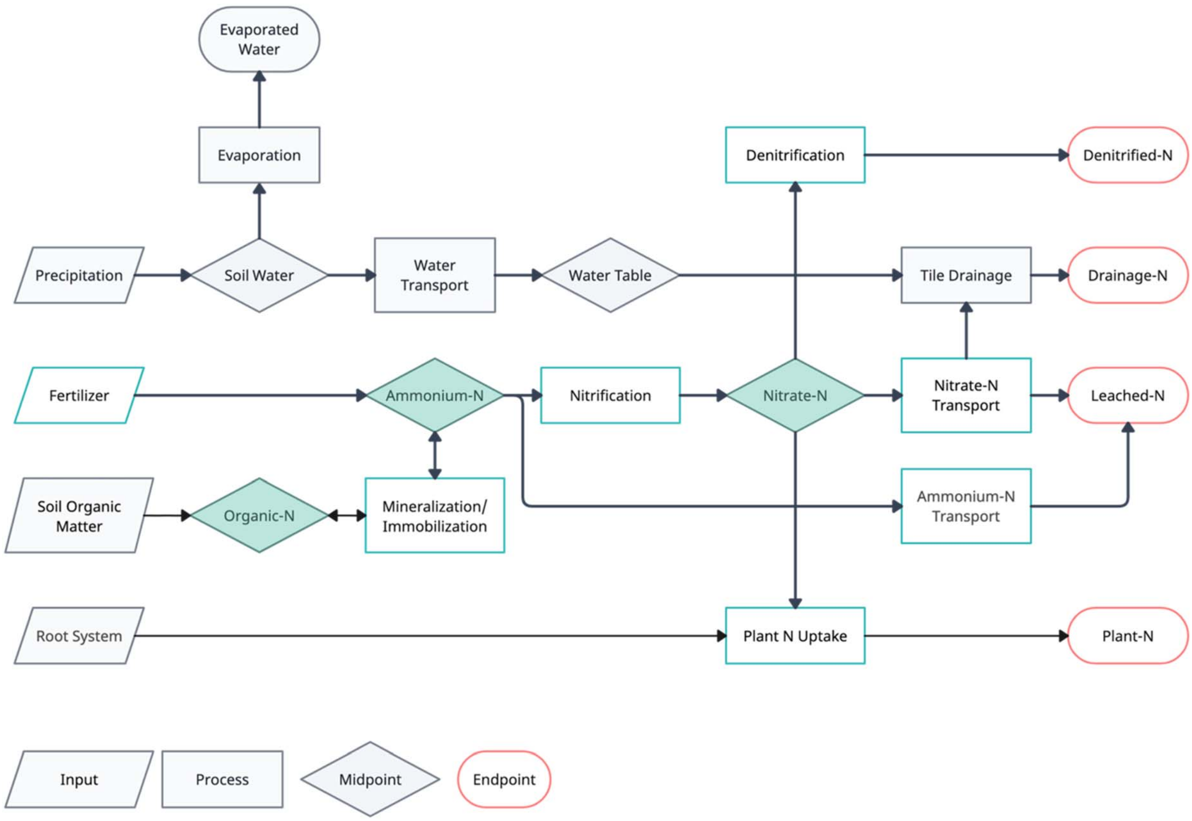

Fig. 1 Model structure, including organization of inputs, processes, intermediates, and output measures. Nitrogen processes are indicated in green. The arrows indicate the flow of data and interactions between intermediates, inputs, and processes to form outputs.

modeled as the area weighted average across the field. The model was written and constructed in MATLAB 2020a.

2.3 Description of model theory

All theory and equations for initializing the soil system, modeling of the transport of water and mineral nitrogen, the biologically mediated transformations of soil nitrogen, the uptake of water and nitrogen by the plant, and the tile drainage of water and mineral nitrogen are either acquired directly or adapted from the Soil and Water Assessment Tool (SWAT). A brief description of the model theory is provided here, and a more comprehensive description is available in the SWAT theoretical documentation.[36]

The soil system was initialized with hydraulic properties and organic matter content from SSURGO as described in Section 2.1. Other information, such as the initial background soil mineral nitrogen and the active portion of organic nitrogen, was based on empirical data collected through the USDA Transforming Drainage Project and SWAT documentation.[36,42] Background soil nitrogen is defined as any nitrogen in the soil prior to fertilizer applications. Fertilizer applications were always modeled as ammonium, which closely matched the anhydrous ammonium and urea ammonium nitrogen (UAN) used at the study site.

Physical transport of water and nitrate in soil was modeled using the hydraulic properties of the soil, including field capacity, saturated water content, and saturated hydraulic conductivity of the soil. Incoming precipitation increases water content in the surface soil layer. Once a soil layer has water content above its field capacity, it drains at a rate dependent on its saturated hydraulic conductivity and drainable water volume. Mineral nitrogen is transported with this percolating water. Evaporation and root water uptake were adapted from SWAT documentation, with calibration to ensure that daily transpiration and evapotranspiration were found to be consistent with literature values for cultivated corn fields (Fig. S3†).[52] We also validated soil moisture across five soil depths (10, 20, 40, 60, 100 cm) using data collected by the USDA Transforming Drainage Project to ensure that these modeled processes were accurate.

The bottom of the soil profile was modeled to be semi-impervious. Thus, percolating water pooled once it reached the bottom of the soil profile and created perched water table. This water table drained from the bottom of the soil profile at a rate consistent with empirical data (Fig. S4†). When the water table had reached soil depths above the tile drain (120 cm), tile drainage is triggered. Soil water from the saturated region at the tile depth is drained at a rate dependent on the height of the water table, the drainable volume of water, and the time required for the soil to drain to field capacity. Mineral nitrogen is transported with water that exits the system through tile drainage.

Biologically mediated transformations of nitrogen (*i.e.*, mineralization/immobilization, nitrification, and denitrification) are controlled by soil moisture, temperature, and organic matter content. Mineralization/immobilization and denitrification rate constants were determined through calibration. Mineralization/immobilization controlled the transformation of active organic nitrogen to mineral ammonium. Ammonium could then undergo nitrification to nitrate. Finally, nitrate could be denitrified to gaseous nitrogen through denitrification, which acted as a sink for nitrogen.

For the simulation of a dynamic and growing corn root architecture, RootBox version 6 was used (Fig. S5†).[38,53–55] Data regarding surface area by depth and extent of the root system were acquired from the RootBox simulation. The root characteristics of the generated 3D architecture, such as surface area and depth, were checked against empirical corn root data to confirm accurate representation of observed plant growth (Fig. S6†). Root growth over time was independent of nitrogen uptake or other environmental parameters. Although this is a simplification of root development processes, there is a lack of sufficient data to make the root growth dependent on environmental and nutrient factors.

Corn nitrogen uptake varies with development, with its greatest demand coming between its six-leaf stage to its tassel development. Corn development is related to accumulated GDD's. Using literature data of corn plant nitrogen content over accumulated GDDs, a logarithmic growth regression model was created (Fig. S7†).[56–58] This regression was then combined with the accumulated GDDs in simulations to determine the potential uptake of nitrogen by the root system by day. The distribution of this potential uptake along the length of the root system was calculated using SWAT theory, which states that uptake decreases exponentially with depth, due to there being greater root density near the soil surface. Actual root uptake was then calculated as the difference between potential uptake and available nitrate by depth. The maximum crop nitrogen content was set to 200 kg ha^{-1}, which was based on empirical data at the site. Thus, if the crop had reached a plant nitrogen content of 200 kg ha^{-1}, its daily potential uptake would fall to zero indicating its nutritional needs had been met.

2.4 Parameter calibration

The model is constructed based on established physical, chemical, and biological processes to estimate outcomes (*i.e.*, the fate and transport of nitrogen) based on input data (*i.e.*, weather and farm management data). The model uses theoretical rate equations, as described in SWAT documentation, that are controlled by parameters, such as process rate coefficients. Some of the rate coefficients that control the rate of physical processes described in this model are not absolute and fall within a range of values that vary depending on local and temporal conditions. Value ranges for these parameters are provided by SWAT. Thus, these parameters must be calibrated to determine their values for the context of the model, thereby reducing uncertainty. To calibrate the model, it is evaluated across the range of parameter values and the model outputs are compared to empirical data collected at the study site. We then use the parameter values that produce the lowest error value between the model output and empirical data. This calibration process is vital to instill confidence in the model outputs.[59]

The calibration process was completed for the mineralization/immobilization, denitrification, evaporation, and plant water uptake rate coefficients. Calibration of the model was completed for each of the ten study years on the baseline scenarios. Calibrated mineralization, denitrification, evaporation, and transpiration coefficients are available in the ESI (Table S1†). Calibrated coefficients minimized error between the simulated plant nitrogen and drainage nitrogen totals and the empirically measured plant nitrogen and drainage nitrogen totals (Table S1†). It was not possible to compare the modeled amount of nitrogen ending in the other fate pools (*i.e.*, denitrified and leached) to observed data due to the absence of empirical data for these fate pools. Following calibration, total evapotranspiration and crop transpiration as determined by the model aligned with literature values for a corn cultivated field in the U.S. Midwest.[52]

2.5 Baseline scenarios and fertilizer management scenarios

All modeled scenarios were from April 1st to October 1st, chosen to mimic a typical growing season at the site. April 1st was the earliest fertilizer was applied over the study years and October 1st was selected as the endpoint since the crop was typically harvested in late September or October. All simulations mirrored the planting date and the fertilizer application method (*i.e.*, broadcasting or injection) and practices (*i.e.*, application timing, application rate, and number of applications) that were used on the farm for each respective study year. In addition, all simulations included the empirical weather data (*i.e.*, precipitation, GDDs, and soil temperature) observed on the farm for each study year.

Baseline scenario simulations were performed in which the nitrogen fate and transport at each study site over each study year were modeled. This scenario was used to establish the baseline performance of nitrogen fertilizer use and the fate of nitrogen under typical management (described in Section 2.1) at the site. These data were then used to compare against other modeled scenarios. Other scenarios investigated include modulating the nitrogen fertilizer application rate (from 100 kg ha^{-1} to 200 kg ha^{-1}) and application timing (from April 1st to June 1st).

For every simulated scenario, the four nitrogen fate pools of plant, drainage, denitrified, and leached, were treated as sinks. Nitrogen in the model was split by source (*i.e.*, from background or from fertilizer). The total amount of nitrogen from each source ending in these fate pools was gathered for each simulation.

2.6 Assessing meteorological correlations

Environmental conditions arising from the weather, including precipitation, storm severity, air temperature, and soil temperature, influence nitrogen fate and transport. Mineral nitrogen (*i.e.*, ammonium and nitrate) is transported by water percolating in soils. Air temperature is an important driver of plant development and therefore plant nitrogen requirements. Air temperature also plays a role in soil water evaporation. Biogeochemical cycling of nitrogen through mineralization, nitrification, and denitrification is controlled by soil water content and soil temperature. Thus, how weather conditions correlate with fertilizer and total nitrogen fate in each of the study years was investigated. The total precipitation over the growing season (TP), cumulative precipitation seven days following fertilizer application (P7), the number of storms and storm intensity during the growing season (S# and SI, respectively), and mean soil temperature over the growing season (ST) were collected for each study year. Spearman's correlation analysis, which analyzes the monotonic relationship between two datasets, was performed between these weather data and the amount of fertilizer in the plant, tile drainage, denitrified, and leachate fate pools (f-Plant, f-Drainage, f-Denitrified, and f-Leachate).

2.7 Nitrogen fertilizer scenario modeling

To determine the impact of varying fertilizer application rate on nitrogen fertilizer fate, scenarios were assessed in which the nitrogen fertilizer application rate was varied within the typical range used for cultivating corn (from 100 kg ha^{-1} to 200 kg ha^{-1}). The application timing and application method, and planting date were unchanged in these scenarios. Secondary applications were removed during these model runs, and the total amount of fertilizer was applied at one time.

To assess the influence of fertilizer application timing on nitrogen fate, we modeled applying nitrogen fertilizer on dates from April 1st to June 1st for each study year. Application rates of 100 kg ha^{-1}, 150 kg ha^{-1} and 200 kg ha^{-1} were assessed for each application time across the years to probe the effects of both fertilizer timing and amount. Application method (*i.e.*, gas injection or broadcasting) was not altered from the practice originally performed each year. Planting date was also left unchanged. Fertilizer was added during a single application (*i.e.*, no secondary applications were considered).

3 Results and discussion

3.1 Nitrogen fate in the baseline scenario

Following calibration of the mineralization/immobilization, denitrification, evaporation, and plant water uptake rate coefficients, plant nitrogen had an RMSE of 4.5 kg ha^{-1} (2.7% error) and drainage nitrogen had an RMSE of 2.3 kg ha^{-1} (12.8% error) compared to the empirical end of growing season values. The fate pools were delineated by the source of nitrogen as either from the applied inorganic fertilizer or background nitrogen (Fig. 2). Background nitrogen, or legacy nitrogen, includes soil mineral nitrogen and nitrogen mineralized from soil organic matter, and fertilizer nitrogen is the inorganic nitrogen applied as fertilizer in each study year. We considered the portion of the total nitrogen measured in each fate pool and plot the total nitrogen applied in that year to demonstrate the variability in application rates and lack of correlation between total nitrogen applied and its fate (Fig. 2).

On average, 42% of plant nitrogen originated from fertilizer, with a high degree of year-to-year variance (as low as 19% and as high as 88%). In addition, the mean nitrogen fertilizer use efficiency (f-NUE), or the portion of applied inorganic nitrogen fertilizer taken up by the plant, was 46%, varying from a low of 13% in 2013 to a high of 92% in 2016. Together these data indicate that fertilizer utilization by the crop is highly

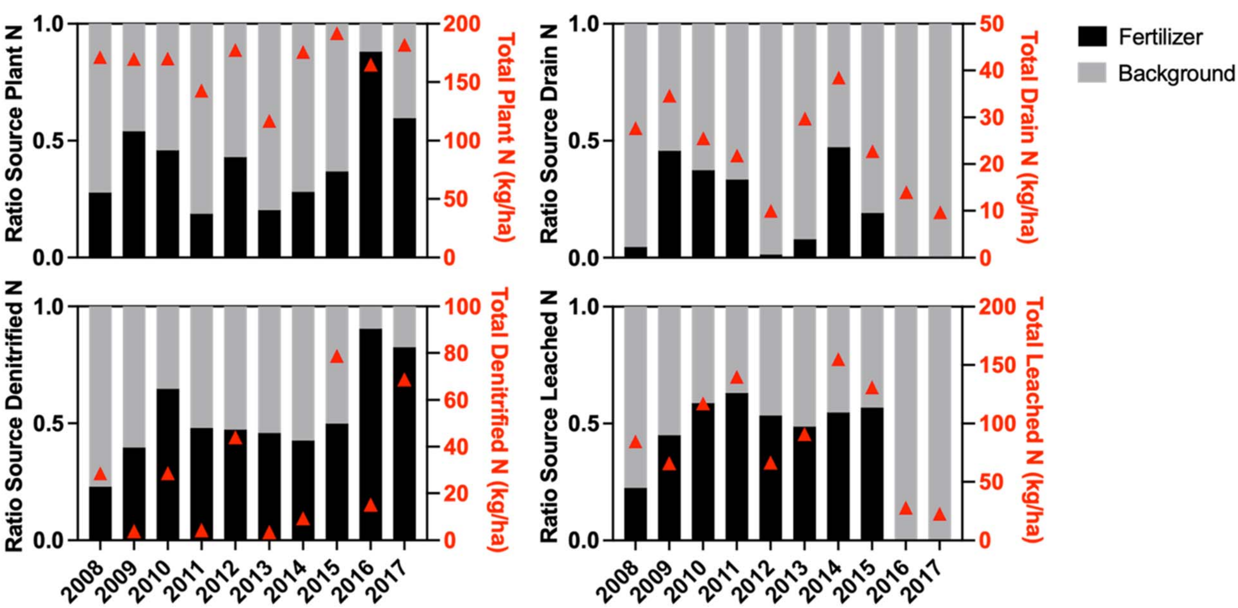

Fig. 2 The portion of applied inorganic nitrogen that ends up in four fate pools: the plant, tile drain, denitrified N, and leached N. The total within each fate pools is divided by the source as either from fertilizer (black) or non-fertilizer soil nitrogen, referred to as background (gray) for each of the simulated years (left *y*-axis). The right *y*-axis (red triangles) presents the total amount of nitrogen in each fate pool across each year. All data are derived from the study site for each year and the respective fertilizer practice.

dependent on year-to-year differences (*e.g.*, fertilizer management and weather). However, total plant nitrogen (*i.e.*, nitrogen from fertilizer and background nitrogen) was found to be consistent across the study period with a with a mean of 166.4 kg ha^{-1}, with the exception of lower values in 2011 and 2013. This indicates that the background pool of nitrogen, which is soil nitrogen from organic matter and legacy mineral nitrogen from prior years' fertilization, is important to meet plant demands and maintain crop nutrition. Previous studies have demonstrated the importance of background nitrogen as a source for crop growth.[60] While the poor f-NUE in the baseline scenario was not found to adversely affect the crop nutrition, it did affect the amount of total nitrogen in leachate and tile drainage. Years with larger total nitrogen loads in drainage and leachate (red, Fig. 2) are driven by inorganic nitrogen fertilizer, where total loads in these fate categories are positively correlated with their ratio of fertilizer (p-value < 0.01 by Spearman's correlation). Thus, managing inorganic nitrogen fertilizer practices to mitigate contributions in leachate and tile drainage is an important goal for protecting water quality.

Total denitrified nitrogen was highly variable across the study years, ranging from 3 kg ha^{-1} to 80 kg ha^{-1}. Denitrification is a biogenic process caused by denitrifying bacteria.[61,62] The rate of denitrification by these microbes is influenced by soil temperature and moisture, which is highly variable during the evaluated period (Fig. S8†).

3.2 Elucidating drivers of nitrogen fate through meteorological correlations

Spearman correlations were calculated between weather data and the amount of nitrogen ending in each of the fate pools (f-Plant, f-Drainage, f-Denitrified, and f-Leachate). Plant nitrogen coming from fertilizer was negatively correlated with TP7 and positively correlated with ST (Fig. 3). Larger amounts of precipitation immediately following fertilizer application will cause rapid transport of inorganic nitrogen fertilizer below the root zone, thus reducing its availability to the plant roots for uptake. Soil temperature corresponds with atmospheric temperatures, where warmer atmospheric temperatures will lead to warmer soil temperatures. Higher temperatures correspond to increased accumulated GDDs and therefore increase the rate of plant development and nitrogen nutritional requirements. Thus, increased daily temperatures will drive the plant to recover more nitrogen fertilizer.

There was a positive correlation between f-Drainage and the number of storms and the mean storm intensity. This follows that more frequent and intense storms lead to transport of inorganic nitrogen fertilizer deep in the soil column concomitant with a high water table causing drainage out of the tile drain. Denitrification of fertilizer was positively correlated with ST. This correlation coheres with the fact that moist soil and warmer soil temperatures are conditions that correspond with accelerated denitrification. Interestingly, the amount of nitrogen fertilizer ending as leachate did not significantly correlate with meteorological conditions. Theoretically, leaching is maximized by increased transport driven by precipitation. Yet too much precipitation will cause a high water table that will trigger leached nitrogen to be exported through tile drainage. The somewhat unintuitive result that f-Leachate does not positively correlate with the precipitation or storm variables, likely arises from the fact that we are unable to disaggregate these competing influences on f-Leachate and the presence of tile drainage at the study sites.

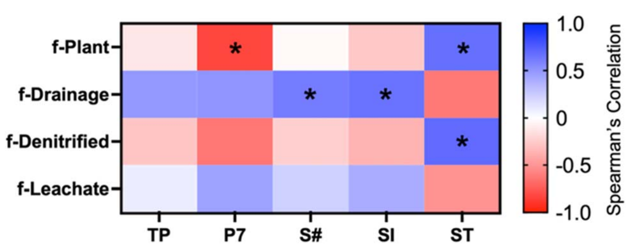

Fig. 3 The Spearman's correlations between the amount of applied inorganic nitrogen fertilizer ending up in each of the four fate pools and the climate variables of total precipitation (TP), total precipitation seven days following fertilizer application (P7), the storm count and mean storm intensity during the growing season (S# and SI), the mean soil temperature during the growing season (ST). Asterisks indicate significant correlations (p-value ≤ 0.05). Correlations were determined from data gathered from the baseline scenario.

3.3 Nitrogen application rate scenarios

While farmers often over-apply nitrogen to minimize risk associated with uncertainties in a growing season and maximize crop yields, there are environmental and economic tradeoffs to this practice. The amount of fertilizer in each fate pool for 100, 150, and 200 kg ha^{-1} scenarios are presented in Fig. 4. As before, increasing nitrogen application rates increased the f-Plant. However, the total amount of nitrogen in all fate pools is increased, meaning that with increased fertilizer applications, nitrogen emissions also increased.

Importantly, reduction in nitrogen applications from 200 kg ha^{-1} to 100 kg ha^{-1} only reduces total plant nitrogen content by 15%. An application of 160 kg ha^{-1}, which is the recommended economic rate for southeastern Iowa based on current fertilizer and grain prices,[63–65] results in 95% of the plant nitrogen content achieved at a higher application rate of 200 kg ha^{-1}. Thus, reducing fertilizer application by 20% only reduces plant nitrogen by 5%. In addition, an application rate of 160 kg ha^{-1} would reduce nitrogen lost to the environment (*i.e.*, fertilizer not utilized by the crop) by 25%. Additional nitrogen added to the system is lost below the root zone due to transport with water (*i.e.*, f-Drainage or f-Leached), or denitrified (*i.e.*, f-Denitrified) before it is accessed by the plant. Thus, in this example fertilizer application reduction would have limited impact on plant nitrogen content but would greatly reduce nitrogen that is lost to the environment. Similar findings are commonly reported in agronomic research.[66–68] It was found that reducing the application rate from 200 to 100 kg ha^{-1} has no effect on f-NUE. This means that reducing application rates has no effect on the efficiency of the system, and only reduces the magnitude of emissions.

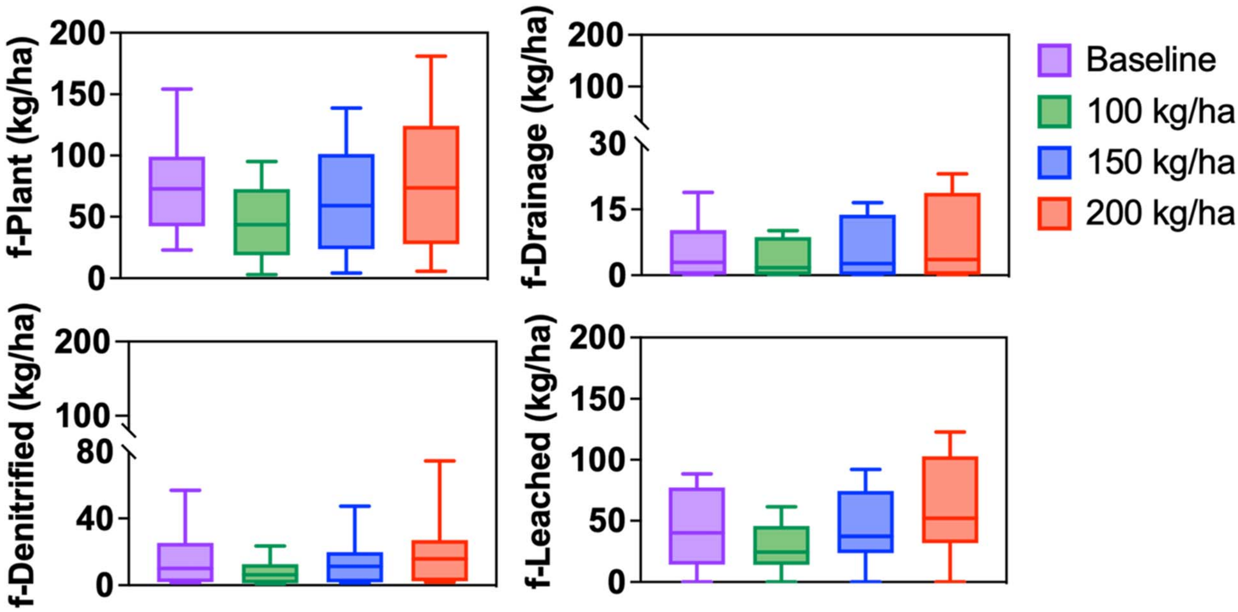

Fig. 4 Boxplot of the area weighted amount of nitrogen ending in each fate pool (*i.e.*, f-Plant, f-Drainage, f-Denitrified, and f-Leached) under the baseline scenario (purple) and scenarios with nitrogen fertilizer application rates of 100 (green), 150 (blue), and 200 (red) kg ha^{-1} across each of the study years at the study site.

3.4 Nitrogen application timing scenarios

The nitrogen demand of corn peaks approximately 5 to 10 weeks after seeds are planted in Iowa.[69] When plant demand for nitrogen is high, uptake rates increase. Thus, timing of nitrogen applications to soils is important so that it is available to match when the crop needs it most. Improved application timing has been described as a way of mitigating poor f-NUE.[70–72]

The ratio of nitrogen fertilizer in the plant (f-NUE) was observed to increase with delayed fertilizer application (Fig. 5A). Benefits of delayed fertilizer application appear to follow a logistic trend, where maximum benefit is reached by delaying application until at least mid-May. The mean f-NUE was found to increase when applied on April 1st, May 1st, and June 1st (means of 0.37, 0.58, and 0.77, respectively). June 1st applications had significantly better f-NUE than applications on April 1st (0.78 compared to 0.38, p-value < 0.05 by One-Way ANOVA, Multiple Comparisons Test), and were found to have significantly higher f-NUE than May 1st (0.78 compared to 0.59, p-value < 0.05 by One-Way ANOVA, Multiple Comparisons Test).

The portion of f-Denitrified (Fig. 5B) was relatively low and constant in comparison to f-NUE, regardless of the fertilizer application date (0.07, 0.08, and 0.15 with applications on April 1st, May 1st, and June 1st respectively). The increase in denitrification began in May, when the soil temperatures surpass 10 °C on average for the years considered. The elevated soil temperatures initiated microbial denitrification processes, resulting in a gradual, linear increase in denitrified nitrogen fertilizer. Significantly more fertilizer was denitrified when it was applied June 1st when compared to applications on April 1st and May 1st (p-value < 0.05 by One-Way ANOVA, Multiple Comparisons Test).

In contrast to these increasing trends, there is a decreasing ratio of f-Drainage and application timing. Inorganic nitrogen fertilizer entering tile drainage can be virtually eliminated by delaying application of fertilizer until May or June. The mean ratio of nitrogen exiting the system through tile drainage was found to fall from 0.12 when fertilizer is applied on April 1st to less than 0.01 when applied on May 1st or June 1st. A similar decreasing trend is observed for f-Leachate, with mean ratios of fertilizer in leachate of 0.26, 0.19, and 0.04 when fertilizer is applied on April 1st, May 1st, and June 1st. Applying fertilizer on June 1st significantly reduced the portion of fertilizer in leachate when it is applied on April 1st and May 1st (p-value < 0.05 by One-Way ANOVA, Multiple Comparisons Test). Delaying application timing until June also significantly reduced f-Leachate from the baseline scenario. It follows that the longer fertilizer application is delayed, the more plant acquired nitrogen and greater denitrified nitrogen, preventing nitrogen transport to soil depths where it is drained or leached. In addition, May and June were the months with the highest average precipitation at the site. Thus, by applying earlier, the nitrogen is more likely to be subjected to greater cumulative precipitation, and therefore transport than if applied later. Delayed application of nitrogen until late-spring has long been a management practice promoted to increase f-NUE and reduce nitrogen emissions to water.[69–72] However, there is a tradeoff of increased denitrified nitrogen that comes with the benefits of delaying nitrogen application. Further, there may be unique situational tradeoffs given the corn growth cycle and depending on a given farm and its location. Nonetheless, delaying application until June reduces the total amount of nitrogen fertilizer lost to the environment.

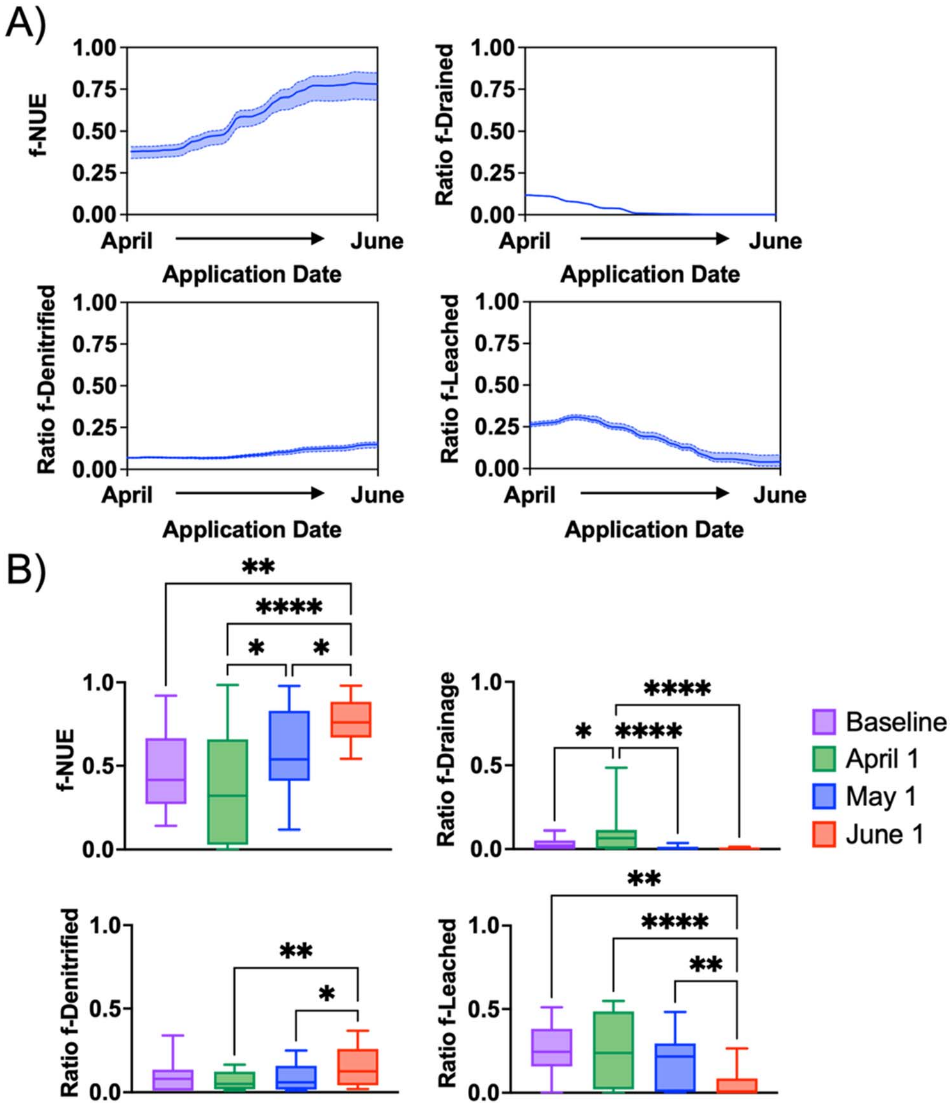

Fig. 5 (A) The mean ratio of applied inorganic nitrogen fertilizer ending in each fate pool across the study years for each of the fertilizer application date scenarios (line). In these scenarios a single application of nitrogen was applied on dates ranging from April 1st to June 1st. Fertilizer applications were tested at three rates: 100, 150, and 200 kg ha^{-1} (shaded area). All other management practices, such as the application method and planting date were unchanged during these scenarios from what was practiced at the study site. (B) Boxplots displaying the mean ratios of total nitrogen fertilizer ending in each fate pool under the baseline scenario (purple) and when fertilizer is applied April 1st (green), May 1st (blue), and June 1st (red). Asterisks indicate significant difference between the means (*p < 0.05, **p < 0.005, ****p < 0.00005).

The benefits of delayed fertilizer application translate to improved economic outcomes. To demonstrate this, we estimated yield from the simulated total plant nitrogen using a regression created using empirical data of plant nitrogen and yield at the study site (Fig. S9†). Estimated yields were then used to calculate net income utilizing current grain and fertilizer prices. The results suggest that the average maximum economic output (*i.e.*, net income per hectare) increases 240% when nitrogen application was delayed from April 1st until June 1st (Fig. S10†). In addition, the application rate associated with the maximum economic output was reduced from 185 kg ha^{-1} to 150 kg ha^{-1} when fertilizer was application was delayed from April 1st until June 1st. Thus, delaying fertilizer application reduces the amount of nitrogen fertilizer inputs needed to reach the economic output obtained with earlier fertilizer applications.

To illustrate the effects of different fertilizer application timings on nitrate depth, we analyzed the mean fertilizer mass by depth across the study years when applied on April 1st, May 1st, and June 1st. We then superimposed the corn plant root surface area at V6 (when nitrogen demand and biomass increase rapidly) and fertilizer by depth to further delineate the impact of application timing (Fig. 6). When fertilizer is applied April 1st, the fertilizer penetrates depths below the V6 root system, such that it is not accessible to the plant when its demand is highest. The later the fertilizer is applied, the more overlap in nitrate availability and root surface area, with near complete overlap of the applied fertilizer nitrogen and V6 root

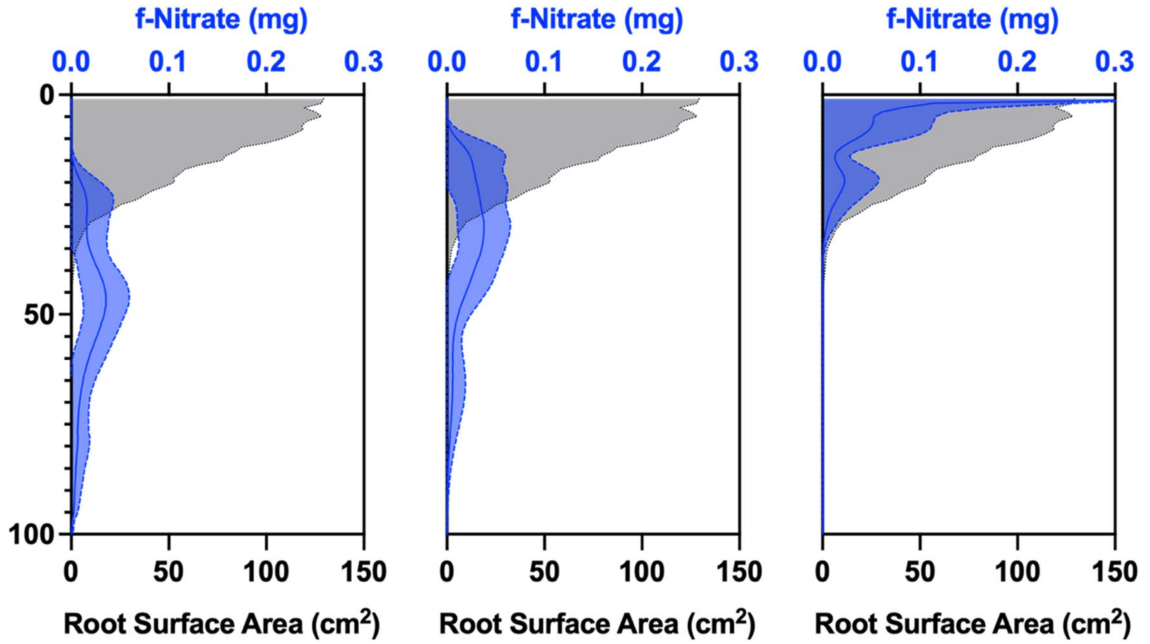

Fig. 6 The simulated mean mass of f-nitrate in the soil by depth below where fertilizer was applied (blue line) and 95% CI (blue shaded area) and the mean root surface area (gray) when the maize plant has reached the V6 development stage. Simulations were performed across the study years with an application of 150 kg ha^{-1} with fertilizer applied on April 1st (left), May 1st (middle), and June 1st (right). All other management practices, such as the application method and planting date were unchanged during these scenarios from what was practiced at the study site.

surface area for the June 1st scenario. These results, again, support that applying nitrogen later allows for greater spatio-temporal overlap with the root system and its developmental demand for nitrogen. As established in the application timing scenarios (*vide supra*), delayed application leads to higher f-NUE and total plant nitrogen while reducing the amount of nitrogen fertilizer in leachate and tile drainage. This visualization clearly demonstrates the importance of the availability of inorganic nitrogen fertilizer for obtaining higher f-NUE and reducing environmental impacts by reducing the amount of fertilizer that can be leached or drained.

3.5 Nitrogen management implications

A primary goal of developing this model was to enable determination of the transport and fate of nitrogen added to soil and intended for crop uptake as a function of soil-crop system characteristics. Given the good agreement of model results with corn farm data set and established knowledge of practices to abate large nitrogen losses due to leaching, the model serves to interrogate perturbations to the system. We are particularly interested in doing so to inform possible avenues for improved nitrogen management on farms. Herein, we present interpretation of our findings to inform interventions to rebalance the crop production nitrogen cycle.

The outcomes of scenarios modeled in this study demonstrate the influence of different management practices on inorganic nitrogen fertilizer fate. The baseline, or status quo, scenario matches conventional wisdom of typical inorganic nitrogen fertilizer application rates and timing: (1) rates do not match the crop needs and (2) weather conditions drive nitrogen emissions. The weather and nitrogen transport and fate are inextricably tied. Further, crop nitrogen uptake, tile drainage, leaching, and denitrification are impacted by precipitation and atmospheric temperature. However, the field of crop production is changing, trends in farming practices are shifting, and the focus on soil health, for example, is emerging. With available data or appropriately generated, representative datasets can be used to interrogate existing and hypothetical scenarios to inform on-farm practices and the design of interventions to improve nitrogen management. Here, we discuss a few ways our results can be interpreted to inform such interventions.

As one would expect, increasing fertilizer application rates led to higher average plant nitrogen content. Adversely, higher rates led to more denitrified (*i.e.*, lost to the atmosphere) nitrogen, tile drainage nitrogen, and nitrogen leachate. Reducing application rates was demonstrated to have limited effects on crop assimilated nitrogen, while substantially reducing the amount of inorganic nitrogen fertilizer wasted. More judicious use of inorganic nitrogen fertilizer (*e.g.*, meeting measured soil needs *versus* conventional overapplication rates) can reduce environmental impacts of crop development while maintaining yields. These findings highlight the importance of real-time (or near real-time) soil nutrient quantification methods, matching crop needs, and evaluating tradeoffs (*e.g.*, economic cost of more inputs, unintended consequences of over-application) when determining fertilization rates. Soil testing, soil sensors used to inform precision agriculture methods, and/or computational tools, such as economic nitrogen rate calculators can aid in providing the data needed to make informed decisions.

Application timing was found to be very influential for nitrogen fertilizer fate. Delayed application increases the probability that inorganic nitrogen added as fertilizer to soil will be present in the root zone when crop development demands it. Increased uptake of inorganic nitrogen fertilizer within the root zone also limits the amount that will be transported to the deep soil where it is leached or exported through tile drainage. Later application of nitrogen agrees with best management literature on how to increase efficiency and decrease emissions yet may not always be practiced for a variety of reasons (*e.g.*, access to equipment that can deliver fertilizer to taller corn plants or other on-farm practical limitations). In addition, poor weather conditions such as heavy precipitation in late-spring could still lead to poor f-NUE even if delayed fertilization is practiced. Interventions that interrupt the nitrogen transport in soil that are governed primarily by water infiltration and encourage long-term availability of nitrogen in the root-zone would greatly improve nitrogen management. Extensive research efforts are directed at developing stimulus-responsive carriers that protect nitrogen in the soil and release it when and where it is needed. Current developed and developing technologies include polymer-based encapsulation or engineered nano sorbents that retard transport and respond to changes in the local environment to release nitrogen when needed by the crops.[25,27,73–76] Additional interventions range in technical complexity, including bioengineered microbes that fix nitrogen to be applied near the crop root system,[77] and reduced-tillage and residue management to boost soil organic matter.[78–80] Soil organic matter with a high carbon to nitrogen ratio stimulates microbial immobilization of mineral nitrogen where it is stabilized as organic nitrogen, which can increase residence time and reduce rapid transport to below the root zone.[81,82] This organic nitrogen could act as a stable pool of nitrogen in the root zone that can be accessed by crops and reduce the need for synthetic nitrogen fertilizer supplements.[79,83,84]

4 Conclusions

We developed a mechanistic model that captures the transport, transformation, and fate of inorganic nitrogen applied to agriculture soil, within a soil-corn plant system. We applied this model to a study site over ten study years to assess how management practices affect the fate of inorganic nitrogen fertilizer and elucidate the influence of variable parameters, year-to-year. Site specific data (*i.e.*, soil parameters, daily weather data, planting dates, and fertilizer management practices) were used to assess the baseline fate and performance (as f-NUE) in the system over the study years. Next, we applied scenarios modulating application rates of inorganic nitrogen fertilizer and application timing. Reducing application rates from 200 kg ha^{-1} to 160 kg ha^{-1} had limited impact on plant nitrogen content, while decreasing wasted nitrogen fertilizer by 25%. Delayed application until June significantly increased the f-NUE and denitrification while reducing the amount of fertilizer leached and exported through tile drainage. This improvement in f-NUE and the reduction of nitrogen originating from fertilizer in leachate and tile drainage was due to increasing the availability of fertilizer in the root zone of the soil when the crop most needed nitrogen. Together, the results from this study support its utility in accurately capturing the intended processes and demonstrate ways to enhance crop nitrogen content while reducing nitrogen losses to the environment. However, achieving the goal of minimizing (or eliminating) inorganic nitrogen inputs is likely not going to be achieved by a single strategy nor will it be a one-size-fits-all solution. Rather, a combination of computational and empirical studies to probe conventional crop agriculture will be immensely beneficial and will inform tractable ways to improve our inefficient, unsustainable use of inorganic fertilizer.

Data availability

Data for this article include the model code, results from the modeled scenarios, and publicly available datasets. The MATLAB code for the model and the results from the modeled scenarios presented herein, can be found at the following GitHub link: **https://github.com/Gilbertson-Lab/Iowa-Corn-Nitrate-Transport**. The data used for the scenario modeling is available in the public datasets outlined in the Methods section.

Conflicts of interest

The authors declare no competing financial interest.

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