Two experiments featuring four different treatments of management practice have been conducted to investigate the environmental and management controls on soil ammonia (NH$_3$) fluxes and nitrate (NO$_3^-$) leaching using the mesocosm facility. In the first experiment, urea was applied to three replicate soil rhizotrons at a rate of 103 kg N/ha before planting of corn seeds (hereafter, treatment 1). To limit soil NH$_3$ availability and better match plant nitrogen (N) demand, in treatment 2, the same amount of urea was equally split into four individual applications. As in treatment 1, the first split was applied before corn planting; the remaining three applications were conducted every 2-3 weeks after corn emergence. In both treatments 1 and 2, urea was sprayed onto soil surface without incorporation. In the second experiment, three replicate soil rhizotrons were respectively fertilized with urea (hereafter, treatment 3) and straw-bedded beef manure (treatment 4) at a rate of 200 kg N/ha. The fertilizers were applied in all before corn planting and incorporated into the soils at 10 cm depth.

Therefore, the four experimental treatment nested in the two experiments differed in terms of fertilizer type, amount and timing of fertilizer application, and whether or not fertilizer is incorporated into the soils, allowing examination of their respective effects on soil NH$_3$ flux. Some of the key results are presented below.

As shown in Fig. 1, soil NH$_3$ emission increased dramatically following the urea applications in treatments 1 and 3 where a single urea application was adopted. Peak NH$_3$ emission was much higher (~40 nmol/m$^2$/s) and lasted much longer in treatment 1 than in treatment 3. In treatment 2, episodes of high NH$_3$ emission were triggered by individual split urea applications (Fig. 1a). However, compared to treatment 1, these fertilizer-induced NH$_3$ emissions were much lower in magnitude and shorter in duration (Fig. 1). In contrast, NH$_3$ flux in the manure-fertilized soils was low (0.065±0.078 nmol/m$^2$/s) throughout the experimental period and did not respond to the manure input. Integrated over the entire measurement
period of each treatment, cumulative loss of NH$_3$ from the fertilized rhizotron soils amounted to 2.80 kg N/ha, 0.81 kg N/ha, 0.19 kg N/ha, and 0.04 kgN/ha, respectively (Fig. 2), corresponding to 2.7%, 0.79%, 0.095%, and 0.020% of the applied fertilizer-N. Therefore, results from these experiments suggest that splitting one-time urea application into individual smaller doses (treatment 2 vs. treatment 1) and incorporating urea into deep soil layers (treatment 3 vs. treatment 1) can help reduce soil NH$_3$ emissions significantly. Moreover, when incorporated immediately following application, applying manure as an alternative source of N fertilizer appears to result in the lowest soil NH$_3$ emission compared to the urea applications (treatment 4 vs. treatments 1-3).

![Figure 1. Soil NH$_3$ fluxes from the fertilized soils under the four treatments. Grey dashed vertical lines denote fertilizer applications. Green dashed vertical lines denote plant emergence.](image-url)
To further explore the mechanisms underlying the distinct soil NH$_3$ emission patterns revealed in these experimental treatments, soil NH$_3$ compensation point was calculated and then compared to the measured NH$_3$ fluxes. In soil pore space, NH$_3$ gas will dissolve in soil pore water (Eqn. 1) and dissociate into ammonium ion (NH$_4^+$) and hydroxide ion (OH$^-$) (Eqn. 2), driving a net equilibrium between NH$_3$ in soil pore air space and NH$_4^+$ dissolved in soil pore water (Eqn. 3).

$$NH_3(g) + H_2O \rightarrow NH_3 \cdot H_2O$$  
Equation (1)

$$NH_3 \cdot H_2O \rightarrow NH_4^+ + OH^-$$  
Equation (2)

$$NH_3 + H^+ \leftrightarrow NH_4^+$$  
Equation (3)

Following Pleim et al. (2013), the equilibrated concentration of NH$_3$ in soil air space can be related to aqueous concentrations of NH$_4^+$ and acidity (H$^+$) in soil water as follows:

$$\chi = \frac{A}{T_s} e^{-B/T_s} \Gamma$$  
Equation (4)

where $\chi$ is the compensation point concentration of NH$_3$ in the soil pore air space (ppb), A ($2.7457 \times 10^{15}$) and B (10,378) are constants derived from the NH$_3$-NH$_4^+$ equilibria constants, T$_s$ is the soil temperature (K), and $\Gamma$ is the dimensionless NH$_3$ availability in soil where $\Gamma = [NH_4^+]/[H^+]$. Thus, $\chi$ is a better indicator of soil NH$_3$ emission potential than commonly measured bulk soil NH$_4^+$ concentration because it accounts for the temperature-dependent partitioning of NH$_4^+$ (which is involatile) and NH$_3$ in soil pore water. $\chi$ was calculated on each soil sampling date throughout the two experiments using T$_s$, NH$_4^+$.
concentration, and pH measured for the 0-30 cm soil layer. A plot of $\chi$ versus the measured soil NH$_3$ fluxes is shown in Fig. 3.

Soil NH$_3$ compensation point was significantly correlated to the measured soil NH$_3$ fluxes in treatments 1 and 3 (Fig. 3), suggesting that hydrolysis of urea that increased NH$_3$ availability in the soil was the dominant driver of the observed NH$_3$ pulses following the urea application. Interestingly, an analysis of covariance (ANCOVA) reveals that the slope of the linear regression between $\chi$ and the soil NH$_3$ flux was significantly higher in treatment 1 than in treatment 3 ($P<0.01$). This significant difference indicates that although the NH$_3$ emission potential in the 0-30 cm soil layer was similar between treatment 1 and treatment 3, there was significantly less NH$_3$ that actually made its way to the atmosphere in treatment 3. This is very likely due to the deeper urea incorporation in treatment 3 which increased residence time of NH$_3$ in the soil pore space, leading to enhanced biological uptake and physical absorption of NH$_3$ in the soils. In contrast to the strong relationship between $\chi$ and NH$_3$ emission in treatments 1 and 3, $\chi$ was consistently low and not correlated to the measured NH$_3$ fluxes in treatment 2 and 4 (Fig. 3). The low $\chi$ values in treatment 2 indicate that the split urea applications designed to better meet plant N demand played an effective role in reducing the soil NH$_3$ availability and thus soil NH$_3$ emissions. Analogously, decomposition of manure N to inorganic N might proceed at a slow rate, resulting in limited NH$_3$ available for volatilization from the manure-fertilized soils. However, it is important to note that about 15% of the applied manure fertilizer was originally in the form of NH$_3$+NH$_4^+$. The measured low $\chi$ values in the manure-fertilized soils might therefore imply that substantial losses of NH$_3$ and NH$_4^+$ might have occurred prior to the manure application. Further studies are needed to investigate how manure pre-treatment and storage affect soil NH$_3$ emission post application. Taken together, the distinct magnitude and temporal patterns of NH$_3$ emission observed in the four treatments can be largely reconciled by the
differences in soil NH$_3$ availability among the treatments, which in turn was directly linked to the experimented management practices.

Figure 4. Temporal variations of soil NO$_3$ concentration in the 0-30 cm soil layer (a and b). Grey dashed vertical lines denote fertilizer applications. (c) Cumulative NO$_3$ leaching under the four experimental treatments.

In all four treatments, nitrate (NO$_3^-$) concentration was consistently high (> 10 mg N/kg) in the 0-30 cm soil layer (Fig. 4a and 4b). In treatments 1 and 3, decline of CH and NH$_3$ emission in the urea-fertilized soils was followed by a considerable increase in soil NO$_3$ concentrations, particularly under treatment 1, indicative of enhanced nitrification (e.g., microbial oxidation of NH$_3$ to NO$_3^-$) rates following the urea hydrolysis. Temporal variations of soil NO$_3$ concentrations were less prominent in treatments 2 and 4 possibly due to the relatively low NH$_3$ concentrations in the surface soils. Nevertheless, despite the differential responses of soil NO$_3$ concentration to the fertilizer applications, the measured NO$_3^-$ leaching fluxes were very similar between treatments 1 and 2 and between treatments 3 and 4 (Fig. 4c). In treatments 1 and 2, NO$_3^-$ leaching fluxes was at an almost constant level throughout the entire experimental period, resulting in a linear increase in cumulative NO$_3$ leaching loss over time (Fig. 4c), whereas in treatments 3 and 4, NO$_3$ leaching fluxes were notably lower after DOY 150 (or one month after the fertilizer applications). Cumulatively, NO$_3^-$ leaching was the dominant N loss pathway in the rhizotron soils, accounting for 114%, 103%, 39%, and 31% of the applied fertilizer N in the four treatments, respectively. The revealed high NO$_3^-$ leaching fluxes imply that soil NO$_3^-$ is a dynamic reservoir co-regulated by highly coupled NO$_3$ production (i.e., coupled hydrolysis and nitrification, mineralization of soil organic matter) and consumption (i.e., leaching and denitrification) processes.
Figure 5. Nitrogen mass balance model for the four experimental treatments. Numbers associated with the input and output fluxes are in units of kg N/ha. The gaseous N loss consists of four component fluxes in the order of NH$_3$, NO$_x$, N$_2$O, and N$_2$. The N$_2$ flux was estimated from the measured N$_2$O flux by assuming a R$_{N2O:N2}$ of 0.25. Net mineralization flux was estimated as the residual of the mass balance between the input and output fluxes.

To gain a better understanding of the dynamic nature of N cycling in the rhyzontron soils, a mass balance approach was used to relate the measured N input and output fluxes. This mass balance model conceptualizes the soil inorganic N pool (i.e., NH$_4^+$ and NO$_3^-$) as an open, continuous flow-through system with competing plant-microbial-soil sinks. Specifically, on a cumulative basis, the model assumes that mass fluxes of N input ($F_{\text{input}}$) and output ($F_{\text{output}}$) of the soil inorganic N pool are balanced, with the residual equal to the net change in the soil inorganic N concentration ($\Delta C$):

$$F_{\text{input}} = F_{\text{output}} + \Delta C \quad \text{Equation (5)}$$

$$F_{\text{fertilizer}} + F_{\text{mineralization}} = F_{\text{uptake}} + F_{\text{gas}} + F_{\text{leaching}} + \Delta C \quad \text{Equation (6)}$$

$$F_{\text{gas}} = F_{\text{NH3}} + F_{\text{NOx}} + F_{\text{N2O}} + F_{\text{N2}} \quad \text{Equation (7)}$$

$$F_{\text{N2}} = F_{\text{N2O}}/R_{\text{N2O:N2}} \quad \text{Equation (8)}$$

In Eqn. 6, $F_{\text{fertilizer}}$, $F_{\text{mineralization}}$, $F_{\text{uptake}}$, $F_{\text{gas}}$, $F_{\text{leaching}}$ are mass fluxes of fertilizer N addition, net mineralization (i.e., decomposition of soil organic matter that converts N bound in organic forms to inorganic N), corn N uptake, total gaseous N loss, and NO$_3^-$ leaching, respectively. $F_{\text{uptake}}$ is directly calculated at harvest using the measured total plant dry weight and total N percentage. $F_{\text{gas}}$ is the sum of cumulative emissions of NH$_3$, nitrogen oxides (NO$_x$), nitrous oxide (N$_2$O), and nitrogen dioxide (N$_2$) (Eqn. 7). NO$_x$ and N$_2$O fluxes were measured concurrently with the NH$_3$ fluxes in all four treatment; we
were not able to measure N$_2$ fluxes. It is therefore assumed that production and emission of N$_2$ from denitrification, the dominant source of N$_2$O and N$_2$ in agricultural soils, can be reasonably estimated using a prescribed ratio that relates N$_2$ fluxes to the measured N$_2$O fluxes (R$_{N2O:N2}$) (Eqn. 8). A R$_{N2O:N2}$ of 0.25 (N$_2$ flux is four times higher than N$_2$O flux) was used here to represent a conservative estimate of N$_2$ emission, given the deduction that the observed low N$_2$O emissions were likely due to a high potential of N$_2$O reduction to N$_2$ in denitrification. We further assumed that the measured soil NH$_4^+$ and NO$_3^-$ concentrations in the top 30 cm soil layer were representative to the entire column of rhyzotron soils so that the net change of the soil inorganic N concentration ($\Delta$C) can be estimated. Finally, with all other terms in the model being directly measured or estimated, the model can be inverted to calculate $F_{\text{mineralization}}$, a flux notoriously challenging to quantify in agricultural soils at field scales.

Applying Eqn. 5-8 to treatments 1 and 2 where $F_{\text{uptake}}$ is available, we found that $F_{\text{uptake}}$ was higher than $F_{\text{leaching}}$, highlighting a low plant N use efficiency and the leaky nature of N cycling in agricultural soils. The estimated $F_{\text{mineralization}}$ was 94 kg N/ha and 85 kg N/ha in treatments 1 and 2, respectively, comparable to the applied fertilization rate (103 kg N/ha). The estimated high $F_{\text{mineralization}}$ provided important implications for management of fertilizer applications. Using labeled $^{15}$N isotope tracers, recent studies have uncovered that recovery of current-year N fertilizer in cereal crops is low (e.g., <40%). This finding leads to the hypothesis that the majority of non-fertilizer N found in crops may come from turnover of soil and crop residue N (Yan et al., 2020). The high $F_{\text{mineralization}}$ revealed in this study supports this hypothesis. In light of the high $F_{\text{mineralization}}$ and $F_{\text{leaching}}$ estimated in our controlled mesocosm experiments, we encourage future studies to revisit the widely held conceptual model that fertilizer is a replacement for N supply from soil organic N turnover and is the sole culprit for leaching of N from agricultural soils.

References:


3.) CHALLENGES ENCOUNTERED. (Describe any challenges that you encountered related to project progress specific to goals, objectives, and deliverables identified in the project workplan.)

4.) FINANCIAL INFORMATION (Describe any budget challenges and provide specific reasons for deviations from the projected project spending.)

We currently have significant funds remaining because my student has had help from a teaching assistantship.

5.) EDUCATION AND OUTREACH ACTIVITIES. (Describe any conferences, workshops, field days, etc attended, number of contacts at each event, and/or publications developed to disseminate project results.)

These research activities are providing education and training opportunities for 1 post doc (Dr. Zhongjie Yu) and 1 graduate student (Lee Miller) and 1 research scientist (Matt Erickson).
This research was presented at the American Geophysical Union Science meeting in December 2019.

We have provided a radio interview (Brownfield Ag News) to increase public awareness of our research and the importance of reactive nitrogen.

We have provided a poster presentation at the recent Ag Expo in January 2020.