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Nitrogen-loaded biochar for environmental management: enhancing nitrogen utilization balance in farmland, mitigating ammonia volatilization, and improving fertilizer efficiency

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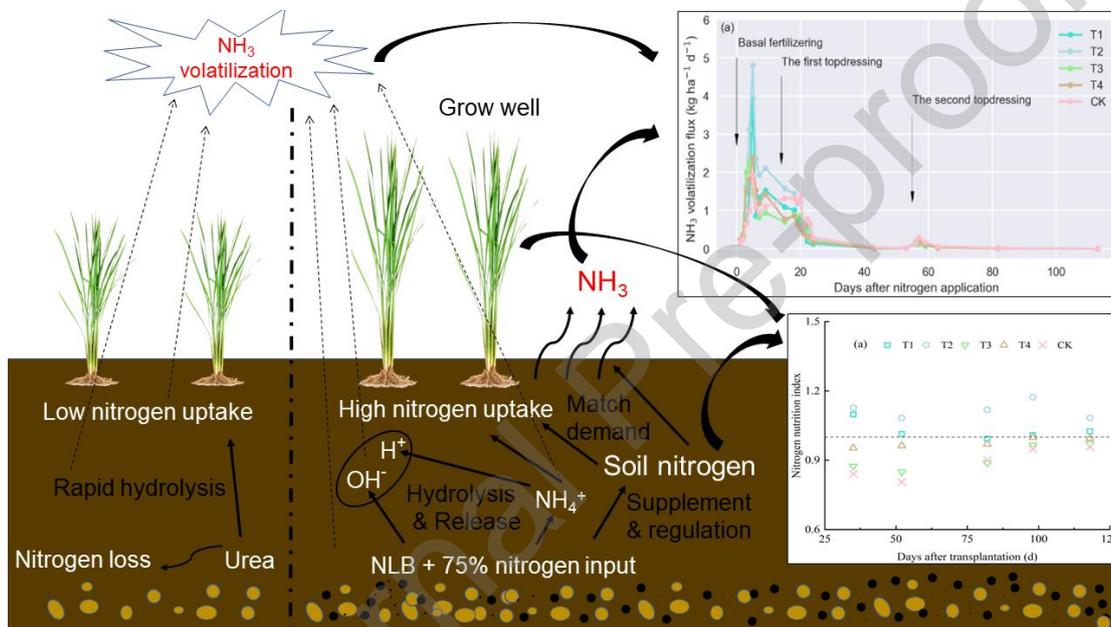
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Abstract: Although biochar was widely applied to improve crop yield, it can also trigger increased ammonia volatilization, thereby deteriorating the environment of rice paddies. Therefore, to continuously supply available nitrogen (N) and mitigate ammonia volatilization in rice fields, a two-year field experiment was conducted with nitrogen-loaded biochar (NLB) combined with less N fertilizer. The treatments included 10 or 20 t·ha⁻¹ NLB+100% urea (T1, T2); 10 or 20 t·ha⁻¹ NLB+75% urea (T3, T4); and a control with 100% urea without NLB (CK). Results indicated the ammonia volatilization accumulation of T3 and T4 treatments was significantly reduced by 13.30–20.96% compared to CK treatment. T2 treatment significantly increased rice yield by 6.94–11.15% and 1000-grain weight by 9.78–11.59%, while the T4 treatment maintained rice yield, due to NLB effectively N compensating and promoting the formation of 1000-grain weight and panicle numbers. Under T4 N management, crop growth and yield were promoted primarily because stable N release better matched the N demands of rice plants in later growth stages. The slow-release N persisted over 30 days in the later stages, increasing soil NH₄⁺-N by 13.72%. The N nutrition index (NNI) of T2, T3, and CK was far from 1, while T4's NNI was close to 1, indicating that T4

provided an optimal N supply. In conclusion, the combination of NLB and 75% N fertilizer effectively mitigated ammonia volatilization in rice paddies and maintains yield stability. This study provided a benefit guidance for agricultural environmental protection in Northeast China.

Graphical abstract



Keywords: Grain yield; nitrogen management; ammonia emission; nitrogen-enriched biochar; less fertilizer application

1. Introduction

Amidst the ongoing expansion of the global populace, there was a marked escalation in the demand for rice (Sun et al., 2019a; Min et al., 2021). Maintaining stable rice yield was crucial for

ensuring national grain supplies and food security in northeast China, the largest commodity grain base in the country. This was especially significant because the paddy rice cultivation area in southern China has declined by approximately 12% between 1999 and 2017, driven by rapid industrial development (Xin et al., 2020). Generally speaking, the most direct way to increase rice yield was to apply high-content nitrogen (N) fertilizers such as urea (Guo et al., 2021). Reports showed that the average N fertilizer input has reached 180 kg ha^{-1} for irrigated rice in China, which was approximately 75% higher than the world average (Fu et al., 2021). Nevertheless, a linear increase in N application did not significantly boost crop yields but can lead to problems like ammonia volatilization, eutrophication, and non-point source pollution (Xu et al., 2023). Therefore, meeting the demand for increased rice production to ensure food security while simultaneously improving resource use efficiency without causing further environmental degradation presented a significant challenge.

The excessive use of chemical N fertilizers meant that not all the N input is utilized effectively, leading to a linear decrease in N use efficiency (Suman et al., 2023). It has been reported that ammonia volatilization from agricultural systems was the primary man-made source of ammonia in the atmosphere, and agriculture-related N loss from ammonia volatilization accounts for 30%–40% of total N input (Liu et al., 2022). Ammonia volatilizations from agriculture have raised significant environmental concerns and pose an economic and ecological challenge in crop farming (Skorupka et al., 2021). Therefore, reducing the total amount and intensity of ammonia volatilization was an urgent priority for agricultural production. Current research suggested that the main ways to reduce agricultural ammonia volatilization included reducing the total amount of N input, adding adsorbent

materials in a field such as biochar, improving fertilization techniques, suppressing soil microbial activity, and adjusting soil pH, etc. Yet, enhancements to fertilization techniques showed minimal improvement in mitigating ammonia volatilization. Suppressing soil microbial activity and adjusting soil pH can have severe negative impacts on soil health and are also cost-intensive by 15% (Mandal et al., 2019; Sun et al., 2021; Wang et al., 2021; Liu et al., 2022). Appropriate N reduction management in paddy fields was one of the most widely used strategies to reduce ammonia volatilization (Guo et al., 2022; Sun et al., 2022). However, the direct reduction of farmland N input was often accompanied by crop growth inhibition, yield decline, and other negative phenomena (Luo et al., 2022). Given this, the application of biochar-modified materials in soils as a N management strategy, building on the advantages of reducing N inputs, was considered an important improvement in paddy field systems (Wu et al., 2020; Lyu et al., 2021). Furthermore, evaluating the N level in paddy fields was a critical issue. The nitrogen nutrition index (NNI) was a quantitative evaluation method constructed based on the accumulation of rice dry matter and N. Numerous studies have shown that the NNI can intuitively assess whether the N supply in paddy fields was appropriate or not (Yang et al., 2000; Li et al., 2022). NNI can evaluate the stability and rationality of new N fertilizer management techniques in supplying nutrients throughout the growth period of crops, which was of great significance for N application in paddy fields and improving N utilization.

Biochar has been widely used in sustainable agricultural production systems because of its multiple advantages, such as increasing soil porosity and decreasing soil bulk density, high recalcitrant carbon content that favors soil carbon sequestration, high cation exchange capacity that may contribute to decreased N leaching, improving soil fertility and crop yields (Bamdad et al.,

2018; Liu et al., 2021; Yin et al., 2021; Zhang et al., 2022). However, biochar was generally alkaline, and the soil pH around it can increase after its application, which can lead to alkaline soils; but for neutral and alkaline soils, increasing soil pH means increasing ammonia volatilization which can further exacerbate N loss (Mandal et al., 2019; Bai et al., 2024). Of course, there were many scholars who used acid-treated biochar to solve the problem of the increase of soil pH and ammonia volatilization in farmland, but the production process of acidified biochar was complex and even contaminates the soil (Sha et al., 2019). Rehman et al. (2020) indicated that a large uncertainty of acidified biochar in the contribution to rice yield was observed with different types of acids. Nitric acid-acidified biochar could increase rice yield by up to 61.8%, while hydrochloric acid-acidified biochar exerted a negative effect on rice yield. These findings showed that a reasonable N loading process can acidify biochar to reduce ammonia volatilization and stimulate greater potential for crop yield increase. Biochar can influence N cycling and ammonia volatilization in soil through mechanisms such as chemical adsorption, physical fixation, ion exchange, surface precipitation, and biodegradation (Hasnain et al., 2023; Zhao et al., 2023). Understanding the characteristics of these mechanisms was crucial for the effective application of biochar loaded with N, as it can significantly reduce ammonia volatilization while promoting efficient N utilization. Among these mechanisms, chemical adsorption and ion exchange are the key mechanisms reducing ammonia volatilization, while physical fixation and surface precipitation help maintain long-term soil N levels (Xie et al., 2024). Biochar can effectively adsorb ammonia molecules onto their surface, reducing their release into the atmosphere indirectly. However, the adsorption capacity was limited and influenced by environmental pH levels (Kohira et al., 2024). Functional groups on the biochar surface can

exchange ions with ammonium ions in the soil, thereby reducing ammonia volatilization. However, the ion exchange capacity can decline over time (Karimi and Soltangheisi, 2024). Biochar may promote the formation of N compounds as precipitates on its surface though this process requires specific conditions (Fan et al., 2023). Biodegradation processes can cause N loss as gases, potentially reducing N use efficiency (Zhang et al., 2023). Ammonium chloride solution was an excellent N-rich solution, and it demonstrated weak acidity because of NH_4^+ hydrolysis (Chen et al., 2020; Chen et al., 2022b). Assuming that biochar was modified by N-rich water, and then applied to paddy fields, which will not only avoid or mitigate ammonia volatilization but also compensate for N deficiency in paddy fields. In this way, N-rich biochar may have some potential to improve rice yield while significantly reducing ammonia volatilization (Markou et al., 2014; Chen et al., 2023). The uncertainty of acidified biochar in the contribution to rice yield will be well solved. Therefore, we highlighted the novel biochar material used in this study was weakly acidic, which prevented severe soil acidification or alkalization and harm to crop growth. Additionally, this biochar was sourced from agricultural fields, making it environmentally friendly and preventing secondary pollution (Rahim et al., 2023). Combined with the advantages of reducing N fertilizer inputs, this N management strategy effectively will suppress ammonia volatilization, enhance N use efficiency, and have positive effects on paddy soil, crop growth, and final yield. Furthermore, there were currently few studies on the stability, rationality, and compensation effects of N supply in the new N management model combining nitrogen-loaded biochar (NLB) with reduced N input, yet these aspects were crucial for reducing ammonia volatilization and increasing crop yield.

Therefore, this study hypothesized that combining NLB with 75% N fertilizer application, as a novel N management model, can reduce ammonia volatilization and enhance rice yield. The specific objectives of this study were as follows: (i) to assess the effectiveness of NLB coupled with 75% N fertilizer in reducing N input, mitigating ammonia volatilization and protecting the agricultural environment; (ii) to explore in depth whether the N can be effectively utilized by crops under this N management model and to elucidate the mechanisms behind yield improvement; (iii) to reveal the mechanism of NLB coupled with 75% N fertilizer on reducing ammonia volatilization using the NNI. This work will provide novel insights and practical guidance for agricultural environmental protection, rice field production, and N utilization in Northeast China.

2. Materials and Methods

2.1 Experimental site and materials

A two-year lysimeter experiment was conducted from June to September in 2020 and 2021 at the Donggang Experimental Irrigation Station (39°52' 48" N, 123° 34' 48" E, 8.1 meters above sea level), Dandong, in northern coastal China (Fig.1). This area was dominated by a humid continental climate with mean annual temperature and average annual rainfall being 7.5 °C and 967 mm, respectively. An automated weather station was used to monitor daily temperatures and rainfall during the two rice growing seasons. In June through September (rice growing season), the maximum and minimum temperatures were 33 °C and 16.6 °C in 2020, and 33.6 °C and 19.3 °C in 2021, respectively. The total seasonal rainfall was 868 mm in 2020 and 802 mm in 2021 (refer to Supplementary Materials, Figure S1). The soil texture in the 0–30 cm layer was silty loam. The fundamental soil properties of this layer at the experimental site were shown in Table 1.

Table 1 inserted here please.

The chemical fertilizers applied were N (urea, pure N \geq 46%, mass fraction, the same below), P (superphosphate, P₂O₅ \geq 12.0%), and K (potassium sulfate, K₂O \geq 50.0%, Cl⁻ \leq 1.5%). The biochar used in this study was pure corn straw biochar with a particle size of around 0.25 mm. It was obtained from Shenyang Longtai Biological Engineering Co., Ltd., Liaoning Province, China. The specific surface area, total pore volume and average pore diameter were 16.16 m²·g⁻¹, 0.20 cm³·g⁻¹, 4.93 nm, respectively. The contents of C, H, O, and N in this biochar were 21.03%, 1.19%, 6.01%, and 2.05% respectively. Its pH was 8.14. Considering the practical operational environment and previously published research literature, the 3.33 kg biochar was placed in a mesh and added to a container containing a 400 L solution of NH₄Cl at a concentration of 1500 mg L⁻¹ when producing NLB (Markou et al., 2014). Following a 2-hour adsorption period, the biochar was delicately extracted and allowed to naturally air dry, resulting in a moisture content of 7.5%. Stirring was performed for a duration of 30 minutes within this time frame. Based on the initial concentration of NH₄Cl solution and the adsorption equilibrium concentration, the N adsorption capacity of biochar was calculated to be 1.01 mg·g⁻¹ (He et al., 2005; Xie et al., 2015). The biochar after adsorption equilibrium was named as NLB. The final pH of the NLB is 5.67. The preparation process was halted once sufficient NLB had been obtained. All the chemical reagents used in the experiment were purchased from Sinopharm Chemical Reagents Co., Ltd.

Fig.1 inserted here please.

2.2 Experimental design and management practices

A lysimeter experiment was conducted over two rice growth cycles in 2020 and 2021 to monitor rice growth and nutrient loss. The experiment was conducted in a completely randomized design with three replicates. Two N fertilizer levels were applied: 100% N fertilizer ($172.5 \text{ kg}\cdot\text{N}\cdot\text{ha}^{-1}$, local N levels) and 75% N fertilizer ($129.4 \text{ kg}\cdot\text{N}\cdot\text{ha}^{-1}$). Five treatments were established as follows: 1) $10 \text{ t}\cdot\text{ha}^{-1}$ NLB+100% N fertilizer (T1); 2) $20 \text{ t}\cdot\text{ha}^{-1}$ NLB+100% N fertilizer (T2); 3) $10 \text{ t}\cdot\text{ha}^{-1}$ NLB+75% N fertilizer (T3); 4) $20 \text{ t}\cdot\text{ha}^{-1}$ NLB+75% N fertilizer (T4); and 5) $0 \text{ t}\cdot\text{ha}^{-1}$ NLB+100% N fertilizer (blank control, CK). Table 2 displayed the application rates of NLB and fertilizer under different treatments. Considering the moisture content of 7.5% during the application of NLB, NLB introduced $11.2 \text{ kg}\cdot\text{ha}^{-1}$ of external N into the paddy field under T1 and T3. Under T2 and T4, NLB introduced $22.4 \text{ kg}\cdot\text{ha}^{-1}$. Each plot was allotted an area of 6.67 m^2 , with a total of 15 plots. Prior to transplanting, NLB was incorporated into the surface soil as a basal fertilizer and thoroughly mixed into the top 15 cm layer through plowing. Japonica rice seedlings (cultivar Dongyan 18) were cultivated in a seedbed, with seed sowing occurring on April 25th. Transplantation took place on May 29th, at a spacing of $14 \text{ cm} \times 30 \text{ cm}$, with three seedlings per hill. It was harvested on 24th September in 2020 and 28th September in 2021. Water management was alternate wetting and drying irrigation mode (Sun et al., 2019b). Weed and pesticide were conducted in accordance with the standards employed by local farmers. Weed management was carried out manually every 10 days, continuing until the grain filling stage.

Table 2 inserted here please.

2.3 Sampling and measurements

2.3.1 Ammonia volatilization

Ammonia volatilization from each plot was assessed using the ventilation method, employing polyvinylchloride (PVC) chambers measuring 30 cm in height and 16 cm in diameter, as detailed by Xu et al. (2012) (Fig. 2). For each measurement, two sponges (2 cm thick and 16 cm in diameter) were pre-soaked in 15 mL of phosphoglycerol solution (comprising 50 mL phosphoric acid and 40 mL glycerol, diluted to 1000 mL) and placed inside each PVC chamber. The PVC chambers were inserted into the soil at a depth of 2 cm, with the lower sponge situated 19 cm above the ground and the upper sponge level with the top of the chambers. The lower sponge functioned to capture ammonia released from the soil, whereas the upper sponge served to block ammonia from the surrounding air. The lower sponge samples were collected daily at 8:00 am. Ammonia absorbed by the phosphoglycerol-soaked sponges within the chambers was promptly extracted using 300 mL of 1 mol·L⁻¹ potassium chloride solution after being shaken for 1 hour, and the resulting extracts were analyzed using a continuous flow autoanalyzer (Autoanalyzer 3, Seal Analytical, Germany). The soil ammonia volatilization flux was calculated as (Sun et al., 2019b; Guo et al., 2021):

$$V = \frac{M}{A \times D} \times 0.01 \quad (1)$$

where V is the daily soil ammonia volatilization flux (kg·ha⁻¹·d⁻¹). M is the average amount of ammonia measured each time by a single device using the ventilation method (NH₄⁺-N, mg), A is the cross-sectional area of the capture device (m²), and D is the time of each continuous capture (d).

During the rice-growing period, the cumulative ammonia volatilization was calculated by integrating the daily ammonia volatilization fluxes during the monitoring period.

Fig.2 inserted here please.

2.3.2 Soil NH_4^+ -N and soil NO_3^- -N

Throughout the rice growing season, fresh soil samples were taken using an auger from depths of 0–30 cm to avoid any interference with N absorption by NLB. The samples were promptly placed in insulated plastic containers, with visible roots carefully removed. The NH_4^+ -N and NO_3^- -N were extracted from 5 g of fresh soil using 50 mL of 1 M KCl solution. The concentrations of inorganic N in the potassium chloride extracts were determined using a continuous flow autoanalyzer (Sun et al., 2019b).

2.3.3 Dry matter accumulation and N concentration

Three representative plants were taken from each plot before harvest. During the tillering stages (TS) and jointing-booting stages (JBS), the plants were divided into stem and leaf. At the panicle-initiation stages (PIS), grain-filling stages (GFS), and maturity stages (MS), they were divided into stem, leaf, and panicle. The plant samples were oven-dried at 105 °C for 30 minutes, then at 75 °C until reaching a constant weight, representing the dry matter accumulation for each rice plant organ. After being ground to pass through a 0.5 mm sieve, the dried samples were digested with H_2SO_4 - H_2O_2 , and the N concentration in the dry matter of the rice plant organs was measured using the Kjeldahl method (Sun et al., 2019b). The N accumulation in various organs of rice and the N concentration of the aboveground rice plant are calculated using the equations (5) and equations (6).

$$NA = NC \times DM \quad (5)$$

$$NC_{\text{aboveground}} = NA_{\text{aboveground}} / DM_{\text{aboveground}} \times 100 \quad (6)$$

where NA represents the N accumulation of various organs ($\text{kg}\cdot\text{ha}^{-1}$), NC represents the corresponding N concentration of various organs (%), DM represents the corresponding dry matter mass of various organs ($\text{kg}\cdot\text{ha}^{-1}$). $NC_{aboveground}$ represents the N concentration of aboveground plant parts (%), $NA_{aboveground}$ represents the sum of N accumulation of aboveground organs ($\text{kg}\cdot\text{ha}^{-1}$), $DM_{aboveground}$ represents the sum of dry matter accumulation of aboveground organs ($\text{kg}\cdot\text{ha}^{-1}$).

2.3.4 Construction and validation of the critical N dilution curve model

The critical N concentration dilution curve models involve the following steps (Justes et al., 1994; Yao et al., 2021; Lacasa et al., 2023): 1) By conducting variance analysis on the aboveground dry matter accumulation and corresponding N concentration values across different treatments, it is determined whether crop growth is limited by N. Based on this, treatments are classified into N-limited and non-N-limited groups. 2) For the N-limited group treatments, a linear curve is used to model the relationship between aboveground dry matter accumulation and N concentration values. 3) In the non-N-limited group treatments, the maximum aboveground dry matter accumulation is indicated by the average accumulation observed in this treatment. 4) The theoretical critical N concentration for each sampling day is determined by the point where the linear curve intersects with the vertical line corresponding to the maximum dry weight on the x-axis. A schematic diagram of the critical N dilution curve is provided in the supplementary materials Figure S2.

The equation of the critical N dilution curve is as follows (Greenwood et al., 1990):

$$NC = a \times DM_{aboveground}^{-b} \quad (7)$$

where NC represents the critical N concentration value (%); a and b are parameters of the equation, where a represents the critical N concentration when aboveground dry matter accumulation is $1 \text{ t}\cdot\text{ha}^{-1}$

¹, and *b*, also known as the dilution coefficient, is a statistical parameter determining the slope of this curve.

Model validation is conducted using the root mean square error (RMSE) and the normalized root mean square error (n-RMSE). The calculation formulas for both can be found in equations (8) and equations (9) (Yang et al., 2000).

$$\text{RMSE} = \sqrt{\frac{\sum_{i=1}^n (P_i - Q_i)^2}{n}} \quad (8)$$

$$\text{n-RMSE (\%)} = (\text{RMSE}/S) \times 100 \quad (9)$$

where P_i and Q_i are the critical N determination values and simulated values respectively; n is the sample size; S is the average value of the measured N concentration. Referring to the standards proposed by Jamieson et al. (1991) to assess model stability, $\text{n-RMSE} < 10\%$ indicates excellent model stability; $10\% < \text{n-RMSE} < 20\%$ indicates relatively good model stability; $20\% < \text{n-RMSE} < 30\%$ indicates moderate model stability; $\text{n-RMSE} > 30\%$ indicates poor model stability.

To quantitatively reflect the N nutrition status of rice, the NNI equation can be constructed based on the critical N concentration variation curve (Lemaire and Gastal, 1997):

$$\text{NNI} = \text{NC}_{\text{aboveground}} / \text{Nc} \quad (10)$$

where Nc is the critical N concentration value obtained based on the critical N concentration dilution model using the same aboveground dry matter accumulation. The NNI can intuitively reflect the N nutrition status within the plant. If $\text{NNI} = 1$, it indicates that the N nutrition of rice plants is optimal; if $\text{NNI} > 1$, it indicates excessive N content in the plants; if $\text{NNI} < 1$, it indicates inadequate N supply within the plant (Huang et al., 2018).

2.3.5 Rice growth and grain yields

To track tillering dynamics, five plants from each plot were marked and monitored for the number of tillers. Observations were carried out every 3 to 5 days prior to the joint-booting stage, followed by 10 to 15 days intervals until grain ripening. At harvest, grain yield was recorded individually for each plot (6.67 m²). Plants were manually harvested using a sickle and threshed with a hand-driven thresher. The harvested grains were air-dried for about one week before measuring the grain yield, which was based on a moisture content of 0.14 kg·kg⁻¹.

2.4 Statistical analyses

Python 3.9.7 was utilized to conduct One-way ANOVA. Tukey's HSD test was employed for multiple comparisons of mean annual values. A p-value less than or equal to 0.05 was considered significant in all analyses. All reported values were the means of three replicates. The path analysis model was used to determine the potential factors affecting grain yields. Figures were created using Origin 2024 and Python-Matplotlib 3.5.1 (<https://matplotlib.org/>).

3. Results

3.1 Ammonia volatilization flux and accumulation

Fig.3 displayed the temporal variations in ammonia volatilization across different treatments in both 2020 and 2021. The ammonia volatilization patterns in 2021 closely mirrored those of 2020. Overall, the ammonia volatilization across these treatments showed a similar trend, peaking in the first week and then progressively decreasing, eventually reaching and maintaining lower levels. The peak daily ammonia volatilization flux occurred approximately 4-5 days after fertilization. Following basal fertilizer application, ammonia volatilization flux increased with the amount of applied N, with

the highest flux observed. In 2020, the ammonia volatilization flux sequence was T2>T1>T4>CK>T3 during the basal fertilization stage. The mean ammonia volatilization flux value for the T2 treatment was $2.13 \text{ kg}\cdot\text{ha}^{-1}\cdot\text{d}^{-1}$. The ammonia volatilization flux of T1 and T2 treatments was higher than that of other treatments. Compared to T2, the average ammonia volatilization flux of T4 decreased by 38.61%. Similarly, the T3 treatment reduced ammonia volatilization flux by 11.92% compared to T1. The average ammonia volatilization fluxes of T1 and T2 treatments were 3.56% and 36.45% higher than that of the CK treatment, respectively. Following the first topdressing, the T3 and T4 treatments exhibited a decrease in ammonia volatilization flux compared with CK treatments, albeit weaker. The flux from the CK treatment was the highest after the second topdressing.

Fig.3 inserted here please.

As shown in Table 3, the accumulation of ammonia volatilization was affected by various treatments throughout the 2020 and 2021 rice growing seasons. The pattern of ammonia volatilization accumulation in 2021 was basically consistent with that in 2020, but the total accumulation of ammonia volatilization in 2021 was apparently lower. Analysis of the table reveals that the initial two fertilizations significantly influence ammonia volatilization accumulation in all treatments, contributing to over 90% of the total. Notably, in the 2020 basal fertilization period, the ammonia volatilization accumulation in the T1 and T2 treatments was significantly higher than in the CK treatment, showing increases of 55.42% and 56.52%, respectively. Compared with T2, the ammonia volatilization accumulation in T4 decreased by 37.08%, and the T3 treatment reduced the accumulation by 44.30% compared with T1. During the first topdressing period, the ammonia volatilization accumulation in T4 was 41.87% lower than that in the T2 treatment, and the T3

treatment reduced it by 40.77% compared with T1. Crucially, ammonia volatilization accumulation in T3 and T4 treatments decreased by 35.60% and 33.77%, respectively, compared to the CK treatment. During the second topdressing period, the ammonia volatilization accumulation in the CK treatment was the highest among all treatments. In the whole rice-growing period, ammonia volatilization accumulation in the T1 and T2 treatments exceeded that in the CK treatment by 25.52% and 28.74%, respectively, whereas in the T3 and T4 treatments, it was notably lower than in the CK treatment by 20.96% and 13.30%, respectively.

Table 3 inserted here please.

3.2 Soil N and its correlation with ammonia volatilization

Fig.4 presented the variations in soil NH_4^+ -N and NO_3^- -N throughout the rice growth periods of 2020 and 2021 under different treatments. In 2020, the NH_4^+ -N content remained high during the initial stages of each treatment (Fig.4a). Compared to the CK treatments, T1 and T2 treatments showed a reduction in NH_4^+ -N content peak by 71.88% and 64.41%, respectively, during the early stage. The T3 and T4 treatments exhibited lower NH_4^+ -N levels. After the second topdressing, the NH_4^+ -N content in T3 and T4 treatments was already 35.29% and 27.30% higher than that of the CK treatment. In 2021, there were also two distinct peaks in the soil NH_4^+ -N content curve (Fig.4b). The most notable feature was that, after 60 days, N levels increased in all treatments except for the CK treatment, where N content decreased. More importantly, the T3 treatment slowly released N over the latter 30 days of whole growth period, leading to a 13.72% increase in soil NH_4^+ -N. T3 treatment notably exhibited the highest N content, thus highlighting the substantial N compensatory effect of NLB.

The curve for NO_3^- -N showed a difference between the two years. Specifically, the NO_3^- -N content in 2020 was maintained at a high level for the first 40 days after basal fertilization application (Fig.4c). At the first peak (base fertilizer stage), NLB treatment had lower NO_3^- -N contents than that of CK treatment. After the second topdressing, the NO_3^- -N content of all treatments showed a decreasing trend, with the CK treatment showing the most significant decrease. Finally, the NO_3^- -N contents of T1, T2, T3 and T4 were 12.09%, 8.35%, 8.61% and 4.43% higher than those of CK, respectively. In 2021, soil NO_3^- -N content exhibited a low trend in the early stage and a high trend in the later stage (Fig.4d). Following the basal fertilizer, the NO_3^- -N content rose to the first peak and then decreased to the lowest point. During this period, the peak of NO_3^- -N content in NLB treatment was generally delayed by three days. After the first topdressing, the NO_3^- -N content also rose rapidly to the second peak. The order of NO_3^- -N content under all treatments from high to low was: CK, T2, T1, T3, T4. After the second topdressing, the NO_3^- -N content of T1 and T2 treatments was even higher than that of CK treatments (19.36% and 40.42%, respectively), but T3 and T4 treatments were 14.36% and 15.90% lower than CK treatments, respectively.

Fig.4 inserted here please.

Fig.5 showed the correlation between soil NH_4^+ -N content and ammonia volatilization flux for the years 2020 and 2021. Both curves exhibited a positive correlation, suggesting that increased soil NH_4^+ -N content correlated with higher ammonia volatilization flux, and this pattern remains consistent over the two-year period. The correlation coefficient was 0.63 for 2020 and 0.60 for 2021 ($p \leq 0.05$). This implied that soil NH_4^+ -N content explained 63% and 60% of the variance in ammonia volatilization flux for the respective years, underscoring its cruciality as an influential

factor. Specifically, during the two years, when soil NH_4^+ -N content was between 0–2 mg L^{-1} , the ammonia volatilization flux was lower. Conversely, with higher soil NH_4^+ -N content (2–4 mg L^{-1}), the ammonia volatilization flux was higher. Equation (11) to (16) represented the processes and products of the transformation in paddy soil of urea N and the NH_4^+ -N carried by NLB into ammonia volatilization and NO_3^- -N. These equations also served as strong evidence of the correlation between soil N and ammonia volatilization. Comparing the two years, in 2021, data points were primarily concentrated in the 0–1 mg L^{-1} range due to the absence of biochar addition in the second year of the experiment, further emphasizing the correlation between ammonia volatilization flux and soil N from another perspective.

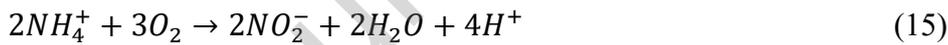
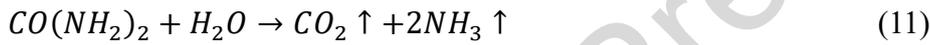


Fig.5 inserted here please.

3.3 Rice dry matter and N concentration

Fig.6 displayed the aboveground biomass and N concentration of various treatments at different growth stages over the two years. Both Fig.6 (a) and (b) illustrated a similar trend of biomass accumulation at each growth stage, with increases correlating with N application. The T2 treatment exhibited the highest biomass accumulation, whereas the CK treatment showed the lowest. In 2020,

the aboveground biomass at various growth stages was higher in the T1 and T2 treatments compared to the CK treatment, with the T2 treatment exhibiting a 27.81% higher aboveground biomass than CK at maturity. However, despite reducing N input by 25%, the accumulation of aboveground biomass in the T3 and T4 treatments was comparable to or even higher than that of the CK treatment. It was noteworthy that the aboveground biomass of other treatments generally exhibited an initial increase followed by a decrease as growth stages progressed, typically declining after reaching peak accumulation at GFS, whereas the T3 and T4 treatments deviated from this pattern (except for the T3 treatment in 2020). Fig.6 (c) and (d) depicted a consistent trend in plant N concentration variation across different growth stages over the two years, gradually decreasing as growth stages progress. TS plants exhibited the highest N concentration, whereas MS plants showed the lowest. There were no differences in the treatment effects on N concentration. In 2020, N concentration varied between 0.67–2.18%, whereas in 2021, it ranged from 0.56 to 2.62%. The dry matter and N concentrations in the two years were basically consistent.

3.4 Critical N dilution curve and NNI

Following the procedure for constructing the critical N concentration dilution curve model (section 2.3.4), a linear relationship between the aboveground biomass and the corresponding plant N concentration was established for each treatment, providing the critical N concentration values for each sampling day. The critical N concentration dilution curve for the entire rice growth period was constructed based on the critical N concentration for each sampling day and corresponding aboveground biomass. The curves and equations for two years were shown in Fig.7. From the figure, the R^2 of the model were 0.982 and 0.972 ($p \leq 0.05$) respectively, indicating that the model can well

explain the relationship between the critical N concentration of rice plants and the aboveground biomass accumulation. Further validation of the model's reliability was conducted using the method outlined in 2.3.4. The aboveground biomass in 2020 and 2021 was substituted into the model to calculate the critical N concentration. Substituting into equations (8) and (9), the RMSE were 0.28% and 0.86% respectively, with the n-RMSE of 14.82% and 22.10% respectively. According to the evaluation criteria, the model demonstrated good stability and was suitable for further application in N nutrition diagnosis. Fig.8 showed the NNI of different treatments over two years. The variation trend of NNI over two years was basically consistent, increasing with N application. Specifically, the NNI of the T2 treatment exceeded 1 at every stage, suggesting that N supply in the T2 treatment was adequate, or possibly excessive. The NNI of the T1 and T4 treatments fluctuated around 1, suggesting that N supply in these treatments was relatively appropriate, meeting the N demand for rice growth. The excessive N supply in T2 treatment also indirectly indicated a key reason for higher ammonia volatilization: over-supply of N lead to poor plant absorption, resulting in gaseous N losses. The NNI of the T3 and CK treatments was consistently below 1 at all stages, suggesting inadequate N supply in these treatments, thus limiting rice growth. However, despite inadequate N supply in the T3 treatment, the NNI approached 1 in the later stages of rice growth, suggesting a reduction in N deficiency severity. The dynamics of NNI over the two years were largely consistent, providing strong evidence for the stability of the experiment.

3.5 Rice yield and yield components

The yield and yield components of each treatment were shown in Table 4. In 2020, compared to the CK treatment, T1 and T2 treatments exhibited significant yield increases of 4.00% and 6.94%

respectively, whereas T3 and T4 treatments showed no significant yield decrease, with T4 even showing a slight increase. T3 treatment decreased yield compared to T1, and the same was observed for T4 and T2 treatments. Apart from the grain number per panicle in the T3 treatment, which was lower compared to the CK treatment, the other treatments exhibited significantly higher grain number. The effective panicle number of each treatment increased compared to the CK treatment, with the largest increase of 15.38% in the T2 treatment. Likewise, the 1000-grain weight increased in each treatment compared to the CK treatment, with the T2 treatment showing the largest increase of 11.59%. In 2021, T1 and T2 treatments showed significant yield increases of 2.52% and 11.15% respectively compared to the CK treatment, whereas the yields of T3 and T4 treatments decreased significantly. In all treatments, the number of grains per panicle increased compared to the CK treatment, with increases ranging from 4.51% to 13.98%. The increase or decrease pattern of the thousand-grain weight aligns with the yield pattern, with increases in the T2 and T4 treatments, and decreases in the T3 and T4 treatments. Comparing the yield between the first and second years, a significant differentiation was observed in the second year, characterized by a significant decrease in yield in reduced N application treatments and significant increase other treatments, which was not observed in the first year.

Table 4 inserted here please.

3.6 Path analysis

In order to further clarify the relationship between yield and other influencing factors such as ammonia volatilization, a stepwise regression method was used to select all indicators in this study one by one, and path analysis was conducted after excluding indicators with insignificant effects (p

≤ 0.05). The results of path analysis were shown in Table 5 ($R^2=0.93$, $RMSE=0.25$). From the table, the direct path coefficients of 1000-grain weight, percentage of filled grains, and NNI on yield were 0.725, 0.457, and 0.646, respectively, indicating that these three indicators had very strong positive effects on yield. The positive effects of 1000-grain weight, NNI, and grain filling rate on yield decrease sequentially. The direct path coefficients of ammonia volatilization accumulation, soil $\text{NH}_4^+\text{-N}$, and soil $\text{NO}_3^-\text{-N}$ on yield were -0.507, -0.241, and -0.238, respectively, indicating that these variates had negative effects on yield. That was, for every 1 unit increase in ammonia volatilization accumulation, soil $\text{NH}_4^+\text{-N}$, and soil $\text{NO}_3^-\text{-N}$, yield will decrease by 0.507, 0.241, and 0.238 units, respectively. From the perspective of indirect path coefficients, the correlation between 1000-grain weight and yield was the strongest, with a correlation coefficient of 0.817, but its direct path coefficient was also the highest at 0.725. This indicated that 1000-grain weight had more direct impact on yield, while the proportion of 1000-grain weight indirectly affecting yield through other variables was very small and controlling the 1000-grain weight of rice to achieve increased yields was an ideal approach. The strength of the correlation between NNI and yield ranked second, with NNI also having a greater direct impact on yield. The correlation coefficient between ammonia volatilization accumulation and yield was 0.715, with its direct impact on yield accounting for 29.32%, and 59.29% through indirect effects of 1000-grain weight and NNI on yield. This also illustrated the importance of controlling ammonia volatilization.

Table 5 inserted here please.

4. Discussions

4.1 The effect of combination of NLB and 75% N fertilizer application on ammonia volatilization

Ammonia volatilization was a major contributor to N loss in rice fields, particularly when excessive N fertilizer is applied (Liu et al., 2020). Many scholars have suggested that N reduction was an effective ammonia volatilization inhibition measure for solving the problem of the paddy environment (Wan et al., 2021; Sun et al., 2022). In this study, combination of NLB and 75% N fertilizer application effectively reduced ammonia volatilization accumulation by 13.30% to 20.96% from paddy fields. And the reduction of N fertilizer application by 25% contributes to a 38.10-41.13% mitigation of ammonia volatilization accumulation. In other words, reducing 25% N fertilizer input played a predominant role in suppressing ammonia volatilization. Yang et al. (2021) also suggested that reducing N fertilizer application could lead to better N utilization and reduce total ammonia volatilization by 50.3%, thus reducing the risk of N loss from rice fields. Reducing usage of N fertilizer was the most effective measure to inhibit ammonia volatilization since it cut off the ammonia volatilization source— $\text{NH}_4^+\text{-N}$. There was a direct relationship between N content and ammonia volatilization. Firstly, reducing N input can reduce ammonia volatilization due to the reactant's reduction, which inhibited the chemical reaction process of ammonia volatilization. Second, diffusion was also an important factor. Lower N concentration in rice field soils and surface water meant less diffusion (Zhou et al., 2022).

NLB has been found to effectively regulate N in paddy soils through its adsorption and desorption characteristics (Chen et al., 2023). In this study, relative to the CK treatment, both the T1

and T2 treatments demonstrated an obvious enhancement in ammonia volatilization flux (Fig.3 (a, c, f, h)) and ammonia volatilization accumulation. This implied an increased risk of ammonia volatilization in paddy fields attributed to NLB. The reasons for this were primarily twofold: one was the balance between weak acid modification (pH=5.67) and the inherent alkalinity (pH=8.14) of biochar. The weak acid (pH=5.67, 20 t·ha⁻¹) effect of NLB was insufficient to offset the inherent alkalinity of biochar, thus posing a slight risk of increasing ammonia volatilization (Chen et al., 2022a). The other was that the increase of soil N sources (NLB) also contributed to a slight risk of increased ammonia volatilization. This observation from above results also substantiated the N compensatory function of NLB. Chen et al. (2019) reported a 2.5-fold increase in surface soil N content due to the effective application of N-rich biochar. Feng et al. (2018) suggested that the increase in N sources in paddy fields was one of the primary contributing factors to elevated ammonia volatilizations. These perspectives lend strong support to the findings of this study. Several studies have demonstrated that biochar and modified biochar can feasibly regulate soil N. Liu et al. (2018) used data compiled across 208 peer-reviewed studies to conduct a meta-analysis. The study concluded that biochar significantly improved plant N uptake (11%), decreased soil N₂O emissions (32%), and mitigated soil N leaching (26%). However, it also presented a risk of elevated soil ammonia volatilization, especially with the use of alkaline biochar (Chen et al., 2022a). Ibrahim et al. (2023) suggested that NH₄⁺-N loss decreased by 22.1% and 10.5% in the soils treated with MgO-bamboo biochar and sepiolite-bamboo biochar, respectively. In this study, NLB could also effectively regulate soil N during rice growth period. Compared with CK, NLB could effectively absorb NH₄⁺-N in soil at the key node (before and after fertilization) and release it slowly in the later stages of rice

growth, thus prolonging the storage time of N in soil (Chen et al., 2023). In this study, the soil N content of T3 and T4 treatments was not apparently lower than that of CK treatments, indirectly indicating that NLB could provide a sufficient supply of soil N. Due to the positive correlation between soil N and ammonia volatilization, NLB may pose a risk of increasing ammonia volatilization.

A crucial contributing factor for ammonia volatilization from paddy fields is soil $\text{NH}_4^+\text{-N}$ content. Liu et al. (2020) reported a positive relationship between soil $\text{NH}_4^+\text{-N}$ content and ammonia volatilization. In our study, we observed a rapid increase in soil N content after the base fertilizer application, with ammonia volatilization peaking within 7 days. Fig.5 also showed a positive correlation between soil $\text{NH}_4^+\text{-N}$ and ammonia volatilization flux in paddy fields. The law of ammonia volatilization and soil N content and the relationship between the two were like previous studies (Yao et al., 2018; Liu et al., 2020; Shi et al., 2023). Furthermore, NLB had a long N release period (Fig.4), which slowed down N release to better match the plant demand for N and improve N uptake at various growth stages, and ultimately reduced ammonia volatilization from rice fields. Pan et al. (2021) have shown that biochar can control the long release of N to reduce the N_2O loss risk and leaching while enhancing the soil fertility. From the perspective of NNI, the T1 and T2 treatments resulted in higher yields but also had significant ammonia volatilization, with NNI values much higher than 1. This phenomenon was not observed in the NLB and reduced N treatments. This indicated that the combination of NLB and reduced N treatments can achieve a more balanced NNI and mitigate ammonia volatilization.

4.2 The effect of NLB on N compensation and rice yields

Biochar possessed favorable physicochemical properties that can significantly improve the soil N content to promote the plant growth and crop productivity (Liu et al., 2021). NLB not only inherited the excellent regulating N properties of ordinary biochar in paddy fields but also effectively compensated for N deficiencies to promote rice growth and yield (Chen et al., 2023). In this study, the analysis results of ammonia volatilization and soil N have effectively demonstrated the supplementation of N content by NLB. On the other hand, it was also easy to demonstrate the N compensation ability of NLB from the perspective of rice dry matter and NNI. NNI was a plant N nutrition diagnostic model based on the critical N dilution curve (Yue et al., 2012), which directly reflected the absorption and utilization of N by plants and indirectly indicates the N nutrition level of the plant environment (Huang et al., 2018). Based on the RMSE validation results, the N dilution curve model established in this study shows strong reliability. Additionally, the parameters of this model were consistent with previous studies (Yao et al., 2021). Therefore, the model results can be used to assess the N nutritional status. Li et al. (2022) suggested that NNI obtained by experimental methods has high accuracy in evaluating the N nutrition status of three major cereal crops (rice, maize, wheat). Fernandez et al. (2022) found that there were many factors affecting NNI, and NNI models based on 4 to 7 samples were ideal for evaluating plant nutrition levels and environmental N levels. In this study, the aboveground dry matter of T2 treatments were apparently higher 27.81% than those of the CK treatment. Equally, a comparison of NNI between CK and T2 revealed variations in N levels in the paddy field ranging from N deficiency to N excess. With the increase in N application, NNI tends to increase, consistent with the findings of Huang et al. (2018)

experiments. The data above all indicated that the application of NLB can compensate for N in rice fields. The path analysis illustrated the associations between NNI, soil N content, and crop yields strongly corroborates this argument. Path analysis revealed how N availability and its efficient use by the plants, as reflected in the NNI, directly impacts crop yield. Moreover, it showed the interplay between soil N levels, maintained or enhanced through the application of NLB, and the resulting yield increases. The data from this path analysis supported the hypothesis that effective N management, facilitated by NLB, leads to improved N use efficiency and consequently higher crop yields. Specifically, the positive correlations between NNI, soil N, and yield emphasized the role of NLB in optimizing N availability and uptake, which in turn enhances plant productivity and grain formation. These findings aligned with previous studies indicating that maintaining adequate matched N levels throughout the growing season was crucial for maximizing yield potential.

N was one of the crucial factors affecting rice growth and development, as well as yield formation (Selvarajh and Ch'ng, 2021). The above content had demonstrated that NLB can supplement N, which was beneficial for rice yield formation. In this study, both T1 and T2 treatments increased yield relative to the CK treatment over two years. Even T4 had slightly increased production. The increase in yield for the T2 treatment ranged from 6.94% to 11.59% over the two years. This indicated that N supplementation of NLB can also have a positive promoting effect on rice yield increase. Indeed, multiple studies have shown that NLB can promote rice yield increase. Cao et al. (2021) found that biochar loaded with urea N could increase rice yield by 12.9%. Ning et al. (2022) added biochar to rice fields with reduced N fertilizer input, and there was no significant decrease in yield in the end. Considering the results of this study comprehensively, multiple reasons

behind the positive effects on rice field production after NLB application based on the literature can be discussed. First, biochar itself was rich in various nutrients such as N and carbon. Biochar was increasingly used for soil quality improvement, and it was an excellent fertilizer in agricultural practices (Oladele et al., 2019; Chew et al., 2020). Sial et al. (2019) discovered that the porous structure and large surface area of biochar particles retained more moisture and nutrients, enhancing the soil's water-holding capacity and increasing N availability for plant uptake, which in turn boosted photosynthesis and crop yields. Biochar had excellent pore structure and strong adsorption, which provided ideal material conditions for carrying nutritive elements. Furthermore, NLB was already loaded with high levels of N before being applied to rice fields, so it carried more nutrients than traditional biochar, which was the main factor ensuring increased rice yield. The assessment results of NNI in this study also provided strong evidence for this. Second, NLB made the distribution of soil N more "even" during the entire rice growth period, especially in the middle-late growth period, where there was a continuous N supply. The matching of soil N supply and rice growth requirements was a positive factor in the accumulation of rice yield (Shaghaleh et al., 2022). In this research, the T3 and T4 treatments did not show a considerable negative influence on rice yield compared to the CK treatment (2020 year). Simultaneously, the curve of soil N concentration in T3 and T4 treatments was smooth relative to CK, and the soil N content was also in the high level at the later stage of rice growth. Rice yield, a comprehensive characteristic among various influencing factors, would better respond to the availability of nutrients and plant productivity over a specific period (Yao et al., 2021). N availability and uptake significantly affected the aboveground biomass of plants by encouraging tillering prior to stem extension. Additionally, the N stored in plant biomass was

redistributed from leaves and stems to support grain formation (Abbruzzini et al., 2019; Ullah et al., 2021). Ali et al. (2020) also reported that the increasing effect of biochar on yield was attributed to the enhanced 1000-grain weight of rice. Our research revealed that NLB accompanied by the reduction of N input had a more significant effect on 1000-grain weight and grain number per panicle. According to the results of path analysis, the correlation between yield and thousand-grain weight was also the strongest, and the direct impact was also the greatest. This fully proves the above conclusion.

5. Conclusion

The research results have strongly supported the initial hypothesis: the combination of NLB and 75% N fertilizer application effectively mitigates ammonia volatilization in rice paddies and maintains yields stability. Given the positive impact of this combination, adding NLB under reduced N conditions is recommended as a feasible N fertilization strategy for rice production aligning with sustainable green agriculture principles. Applying 20 t·ha⁻¹ of NLB with 75% chemical N fertilizer in rice fields reduced ammonia volatilization accumulation by 20.96% while simultaneously stabilizing rice yields. The application of NLB in rice fields significantly increased yields by 11.15%, even with reduced 25% urea use, without compromising yields. This yields increase was primarily attributed to NLB's ability to effectively compensate for N, enhance dry matter accumulation by 27.81% and 1000-grain weight by 11.59%, and release N slowly in the later stages of 30 days to increase soil NH₄⁺-N by 13.72%. Additionally, NNI indicated the N management strategy combining NLB with 75% N fertilizer provided an adequate N supply, meeting crop N demands without leading to excessive gaseous N losses. This was a vital factor in achieving efficient N utilization. Therefore, the

combination of NLB and 75% N fertilizer application is an effective N management model to gain the double benefits of agricultural environment protection, high N use efficiency and rice yields in northeast China. Future research will explore loading N from real-world sources, like eutrophic water, onto biochar for agricultural use, further promoting sustainable agriculture through waste resource recycling.

CRedit authorship contribution statement

Hongyang Chen: Experiment design and execution, Conceptualization, Methodology, Validation, Formal analysis, Investigation, Data curation, Writing - original draft, Writing - Review & editing, Visualization. **Hanmi Zhou:** Investigation, Methodology, Writing - Review & editing, Visualization. **Yang Sun:** Experiment execution, Validation. **Xiaolong Liu:** Experiment execution. **Qi Wu:** Conceptualization, Methodology, Validation, Writing - Review & editing, Supervision, Project administration, Funding acquisition. **Daocai Chi:** Resources, Supervision, Project administration, Funding acquisition.

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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Figures captions

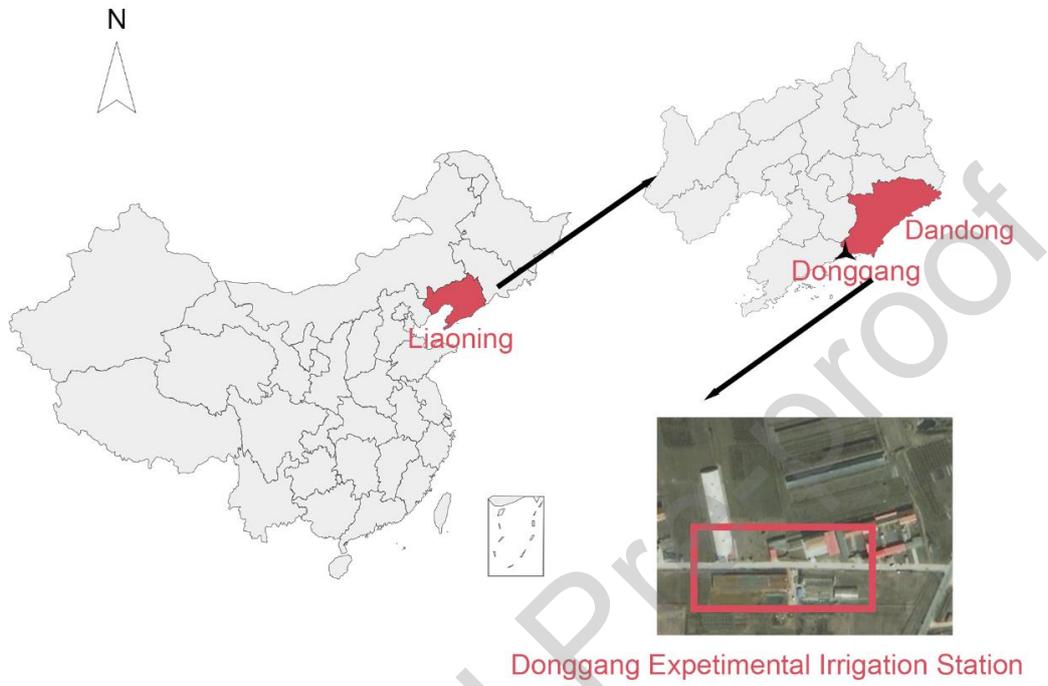


Fig.1 Location of the experimental field at Donggang, Liaoning, China.

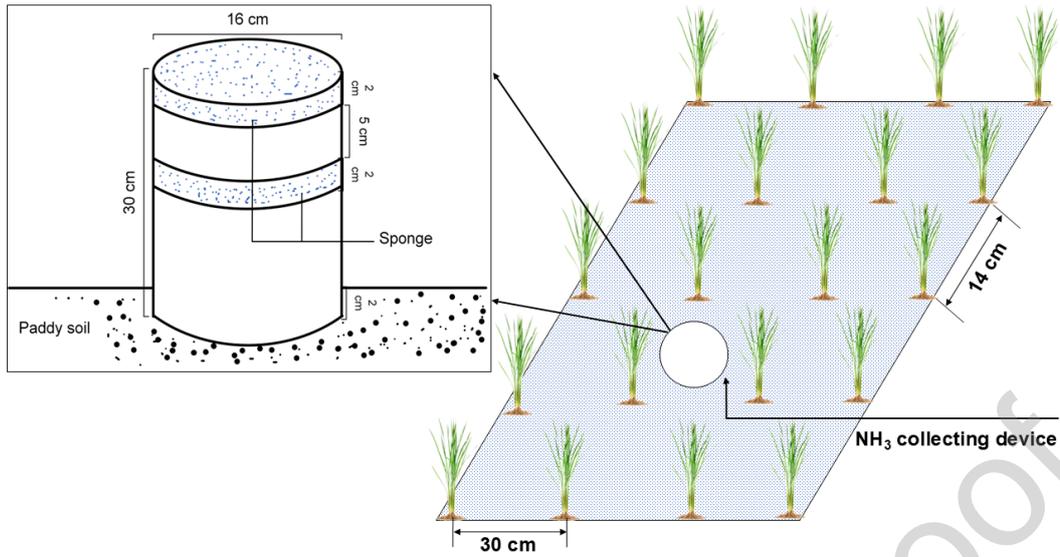
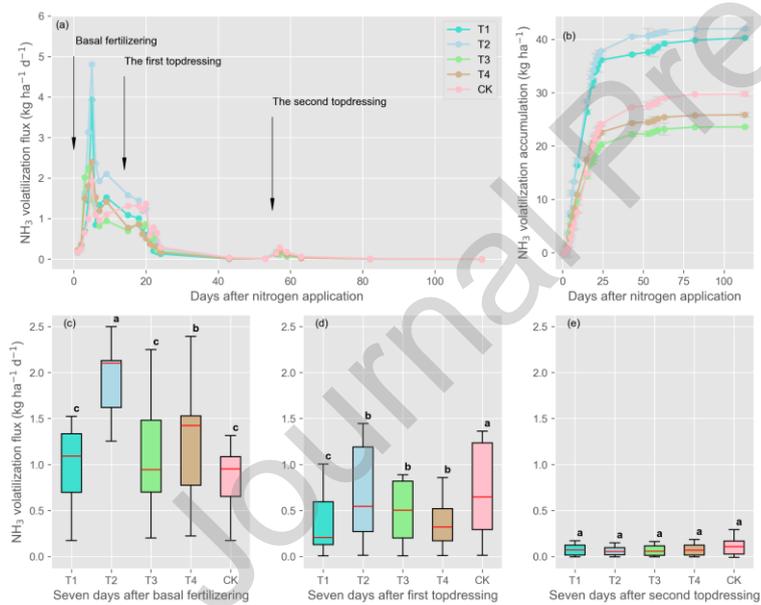


Fig.2 Diagram of ammonia collection apparatus and its position in field plots.



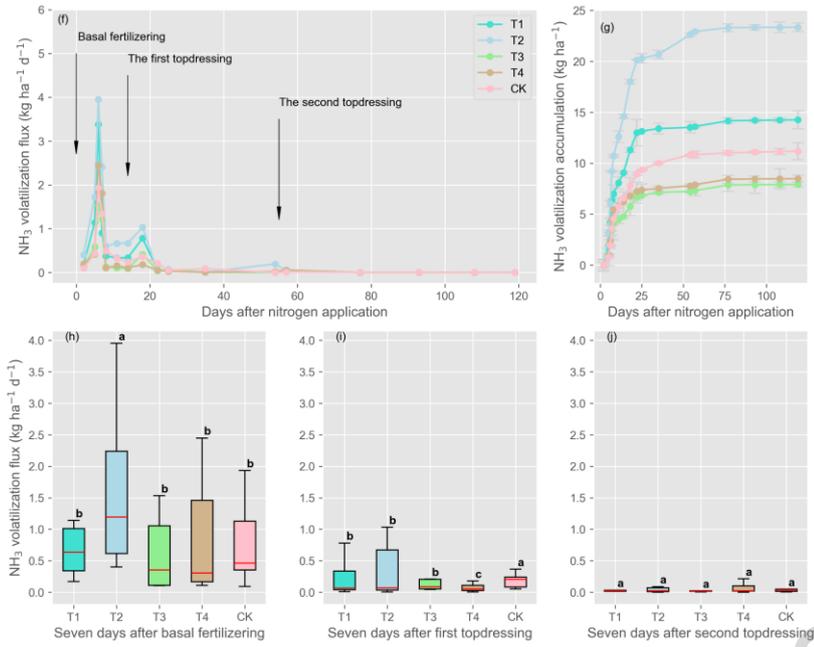


Fig.3 Daily ammonia volatilization flux under different treatments in 2020 (a, c, d, e) and 2021 (f, h, i, j) and ammonia volatilization accumulation trend in 2020 (b) and 2021 (g), respectively. Means with different letters are significantly different at the $p < 0.05$ significance level.

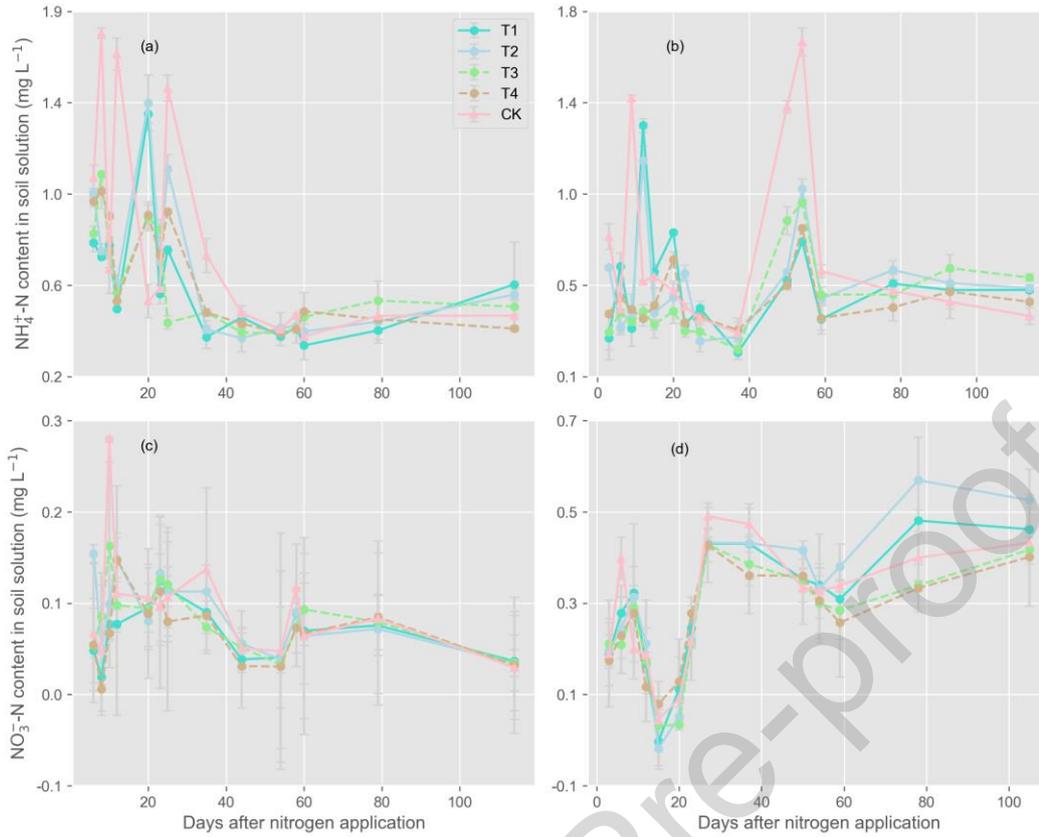


Fig.4 Dynamics of soil NH₄⁺-N (a, b) and soil NO₃⁻-N (c, d) under various treatments in the 2020 (a, c) and 2021 (b, d) rice-growing period, respectively.

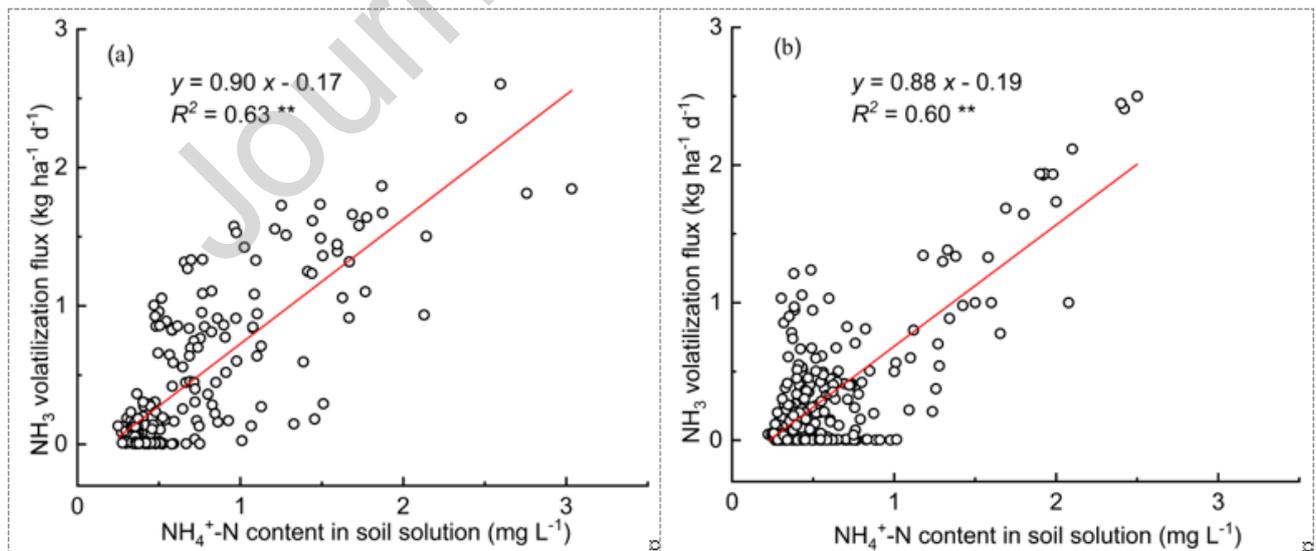


Fig.5 The relationship between ammonia volatilization flux and soil NH₄⁺-N content in 2020 (a) and 2021 (b), respectively.

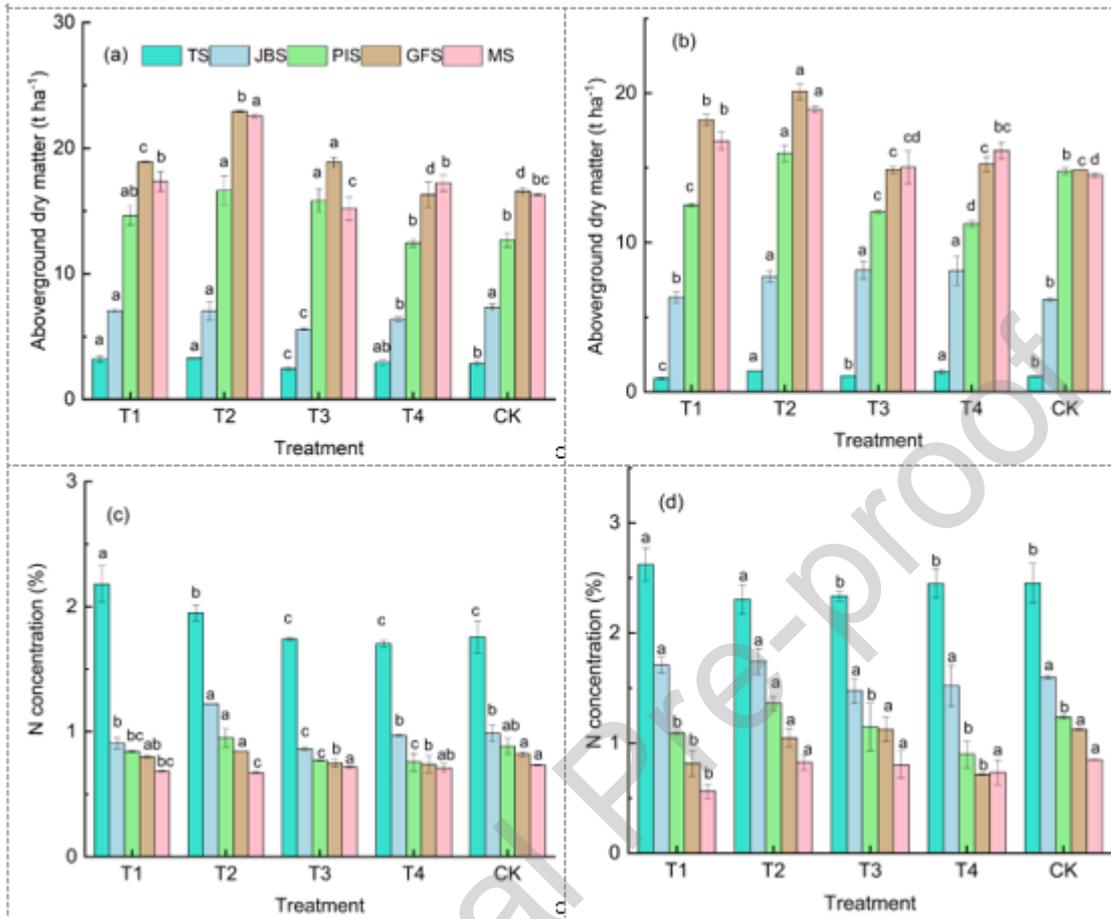


Fig.6 The aboveground biomass accumulation under various treatments at different stages in 2020 (a) and 2021 (b) and plant N concentration under various treatments at different stages in 2020 (c) and 2021 (d), respectively. Means (columns) with different letters are significantly different at the $p \leq 0.05$ significance level.

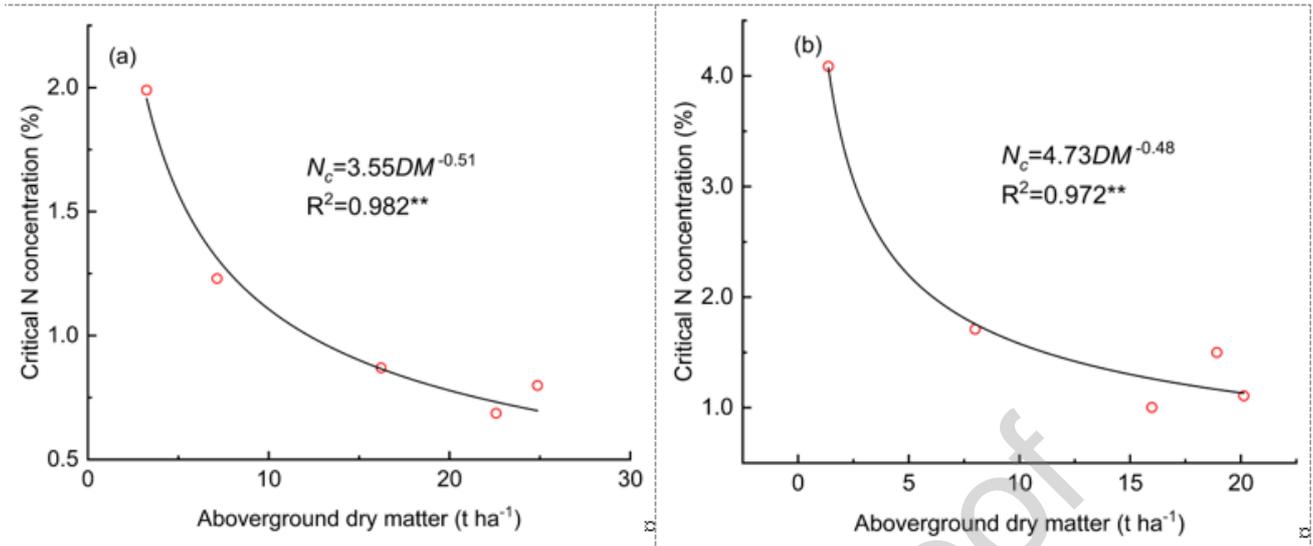


Fig.7 The critical N dilution curve of rice in 2020 (a) and 2021 (b), respectively.

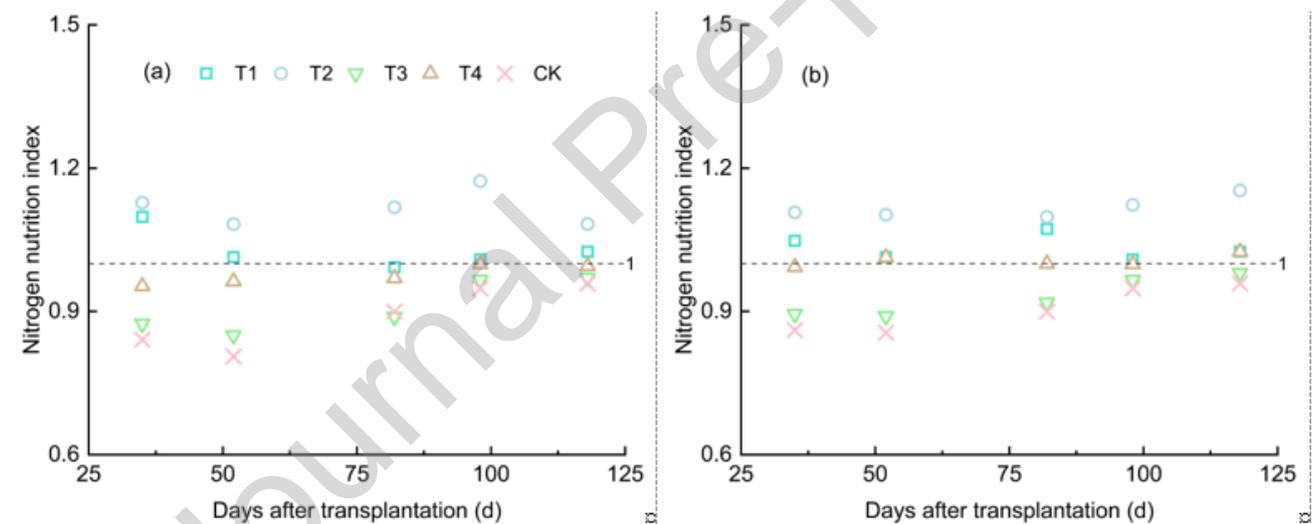


Fig.8 The NNI dynamics of various treatments in the 2020 (a) and 2021 (b) rice-growing period, respectively.

Tables

Table 1 The fundamental soil properties of 0–30 cm layer at the experimental site

Soil properties	Content
Sand (%)	11.4
Silt (%)	66.7
Clay (%)	21.9
pH	6.55
Bulk density ($\text{g}\cdot\text{cm}^{-3}$)	1.50
Available phosphorus ($\text{mg}\cdot\text{kg}^{-1}$)	16.08
Available potassium ($\text{mg}\cdot\text{kg}^{-1}$)	56.56
Total N ($\text{g}\cdot\text{kg}^{-1}$)	0.83
Organic matter ($\text{g}\cdot\text{kg}^{-1}$)	15.33

Table 2 The application rates of NLB and fertilizer under different treatment

Treatment	NLB (kg·ha ⁻¹)	Basal fertilizer (kg·ha ⁻¹)			The first topdressing (kg·ha ⁻¹)	The second topdressing (kg·ha ⁻¹)	
		N	P	K	N	N	K
		T1	11.2	86.25	75	30	51.75
T2	22.4	86.25	75	30	51.75	34.50	30
T3	11.2	64.69	75	30	38.81	25.88	30
T4	22.4	64.69	75	30	38.81	25.88	30
CK	0	86.25	75	30	51.75	34.50	30

Note: NPK denotes the contents of nitrogen, phosphorus, and potassium, which are subsequently converted into corresponding fertilizer contents before being applied to paddy fields.

Table 3 Ammonia volatilization accumulation at various fertilization period under different treatments during the 2020 and 2021

Treatment	ammonia volatilization accumulation (kg-ha ⁻¹)							
	Basal fertilization		The first		The second		The whole rice-	
	period		topdressing period		topdressing period		growing period	
	2020	2021	2020	2021	2020	2021	2020	2021
T1	16.93a	9.07b	21.78a	4.33b	1.57b	0.86b	40.28a	14.26b
T2	17.34a	14.61a	23.31a	6.08a	1.46b	2.68a	42.10a	23.35a
T3	9.43b	4.76c	12.90b	2.38d	1.38b	0.78b	23.71c	7.92c
T4	10.91b	6.22bc	13.55b	1.31d	1.55b	0.95b	26.01c	8.49c
CK	7.54b	6.49bc	20.03a	3.26bc	2.43a	0.45b	30.00b	10.19b

Note: Means followed by the same letter within the same column are not significantly different at $p \leq 0.05$ by Tukey's HSD test.

Table 4 Grain yield and components under different treatments during the 2020 and 2021

Treatment	Yield (kg·ha ⁻¹)	Panicle numbers (hill ⁻¹)	Grain numbers (Panicle ⁻¹)	1000-grain weight (g)	Panicle length (cm)	Percentage of filled grains (%)
2020						
T1	7380.38ab	34.49b	167.80b	23.97ab	16.75	90.63
T2	7613.99a	37.50a	179.82a	24.08a	16.90	91.99
T3	6889.20c	32.53c	155.78d	23.31c	16.88	90.13
T4	7152.44bc	35.00b	162.60c	23.55bc	16.65	91.22
CK	7085.76c	32.50c	156.28d	21.29d	16.69	91.91
2021						
T1	7775.24a	36.20a	168.27b	32.54b	17.30	97.11d
T2	8530.47a	35.88a	176.77a	33.67a	17.95	98.34a
T3	6868.71c	33.45ab	159.73c	28.79d	17.57	97.75b
T4	6971.57c	31.94b	159.25c	29.30d	16.95	97.59bc
CK	7578.97b	33.75ab	152.06d	30.38c	17.48	97.22cd

Note: Means followed by the same letter within the same column are not significantly different at $p \leq 0.05$ by

Tukey's HSD test.

Table 5 Direct and indirect path coefficients of yield and related influencing factors

	X1	X2	X3	X4	X5	X6	Y
X1	0.725	0.063	0.342	-0.338	0.011	0.014	0.817
X2	0.100	0.457	0.340	-0.160	-0.109	-0.109	0.520
X3	0.383	0.241	0.646	-0.425	-0.059	-0.034	0.752
X4	0.483	0.145	0.542	-0.507	0.023	0.030	0.715
X5	-0.033	0.206	0.159	0.048	-0.241	-0.069	0.069
X6	-0.041	0.209	0.092	0.063	-0.070	-0.238	0.015

Note: X1, X2, X3, X4, X5, X6, Y, represent 1000-grain weight, Percentage of filled grains, NNI, Ammonia

volatilization accumulation, Soil NH₄⁺-N, Soil NO₃⁻-N, Yields. Bold numbers indicate direct path coefficients. The

Y column shows the correlation coefficients between each variable and Y.

Declaration of interests

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.

CRedit author statement

Hongyang Chen: Experiment design and execution, Conceptualization, Methodology, Validation, Formal analysis, Investigation, Data curation, Writing - original draft, Writing - Review & editing, Visualization. **Hanmi Zhou:** Investigation, Methodology, Writing - Review & editing, Visualization. **Yang Sun:** Experiment execution, Validation. **Xiaolong Liu:** Experiment execution. **Qi Wu:** Conceptualization, Methodology, Validation, Writing - Review & editing, Supervision, Project administration, Funding acquisition. **Daocai Chi:** Resources, Supervision, Project administration, Funding acquisition.

Highlights

- NLB can effectively replace 25% urea.
- NLB coupled with 75% N fertilizer mitigated ammonia volatilization by 13.30-20.96%.
- NLB slowly released N over 30 days, matching the N demands of rice plants well at late stages.
- NLB with 75% N fertilizer decreased ammonia volatilization and increased yields by improving N utilization balance.

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