

Article

Effect of Deep Placement of Large Granular Fertilizer on Ammonia Volatilization, Soil Nitrogen Distribution and Rice Growth

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Abstract: Excessive fertilization is often applied to produce rice. To reduce nitrogen loss and improve nitrogen use efficiency (NUE), we studied the effects of application depth (surface application, 5 and 10 cm) and shape of nitrogen fertilizers (row application and deep application of large granular fertilizer) on rice growth, soil N distribution and ammonia volatilization. The results showed that grain yield, shoot biomass and total dry biomass of the treatment with N in large granular fertilizer applied at 10 cm depth were significantly higher than those of all other treatments. Moreover, compared with the surface application, the N recovery efficiency and the N agronomic efficiency of deep application treatments were enhanced by 18.1–52.3% and 35.6–95.6%, respectively. Deep application significantly increased $\text{NH}_4^+\text{-N}$ concentration at their fertilization points. During the growth season, N in large granular fertilizer treatments (mixed with clay to form an unusually large pellet of 1.0–1.5 cm in diameter) distributed closer to the roots, while N in other treatments, including row application treatments, was more widely distributed. Compared with the surface application, deep application significantly reduced NH_3 volatilization and $\text{NH}_4^+\text{-N}$ concentration in surface water by 58.7–64.8% and 26.0–72.5%, respectively. Furthermore, the NH_3 volatilization from large granular treatment was 7.6–11.0% lower than that in the row application. In conclusion, applying N in large granular fertilizer at 10 cm depth reduces ammonia volatilization, and improves rice growth and grain yield, indicating improved NUE and lowered environmental risks.

Keywords: rice; deep application; nitrogen; biomass; NH_3 volatilization

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1. Introduction

Rice is the staple food for approximately 65% of the Chinese population [1,2]. Nitrogen (N), as one of the most essential elements for the growth of crops, is of great importance for food production [3,4]. Nitrogen application in China averages 305 kg N per ha compared to 74 kg N per ha worldwide [5]. Currently, ammonia emissions in many countries (e.g., China, India), are increasing, with agricultural activities (e.g., fertilizer application) contributing much to atmospheric ammonia. Globally, an average of 18% of N fertilizer is lost through ammonia emissions [6]. However, an overdose of N application did not further increase the crop yield; rather it decreased the N use efficiency (NUE). In single-season rice cultivation, NUE was only 25–30% [7,8]. This is often attributed to the improper fertilization methods that lead to large amounts of N losses in the environment, and consequently cause environmental pollution and trigger a series of environmental problems [9].

Reactive nitrogen can move into water and the atmosphere through runoff, leaching, and gas evaporation [10], and further cause soil degradation, water eutrophication, groundwater pollution, and ammonia pollution, as well as the greenhouse effect [11,12]. Among these N-related problems, ammonia volatilization is a major pathway of N loss in China, accounting for 14.4–21.0% of total N applied [13]. Ammonia in the atmosphere can react with gases such as sulfur oxides and nitrogen oxides, and thus accelerate the formation of haze, effective haze mitigation is achievable by control measures of NH_3 , nitrogen oxides, and sulfur oxides emission [14]. Haze can gather near-surface aerosols, reducing atmospheric visibility and exacerbating air pollution, adversely affecting people's health and socio-economic development [15]. To improve the NUE, and thus reduce the negative environmental impact as well as ensure the economic benefits of farmers, many new and practical N applications methods, e.g., urease/nitrification inhibitor incorporation [16], controlled release fertilizer [17], and deep fertilization methods [18], have been proposed.

Nitrogen application method greatly affects rice production and NUE. Deep fertilization is an effective way to reduce N loss. Depth normally considered a range: >5 cm [19–21]. Nutrients required can be located near the root zone, which reduces the N loss and enhances the N uptake, and therefore improves rice yield and NUE [22,23]. Some studies have shown that deep application can provide a high NH_4^+ -N concentration for plants and prolong the availability of N [24]. Therefore, compared with surface fertilization, deep fertilization can not only delay the release of fertilizer, but also provide essential nutrients in the critical period for plants [25]. However, most of the previous studies described the distribution of N in rice fields after seeding, but the N distribution during the main growth period for rice remains unclear [18]. In China, the scale of ecological agriculture in paddy fields is increasing. Aquatic animals are cultivated in paddy fields to achieve 'one water and two uses' and maximize the benefits of land resources [26]. However, most of the nitrogen produced by farmland fertilization, residual feed, animal manure, and so on exists in the form of ammonia, resulting in deterioration of water quality and affecting animal growth [27,28]. Some previous studies investigated the technologies of adsorbed ammonia nitrogen in surface water by changing feed and planting aquatic plants to achieve a safe concentration in aquaculture water quality [29,30]. However, it is still unclear to fundamentally reduce the ammonia nitrogen concentration in surface water to ensure the growth of aquatic animals.

Large particle fertilizers cost lower than controlled-release fertilizers. Compared with slow and controlled fertilizer, large particle fertilizer does not add polluting materials [31]. Herein, the objectives of this study were to investigate the impacts of the deep application of large fertilizer granular [32] and fertilization depth on the growth of rice, N distribution in soil profile, and the ammonia volatilization from rice field.

2. Materials and Methods

2.1. Experimental Location and Materials

Pot experiments were conducted at Yunyuan Base of Hunan Agricultural University, Changsha County, Hunan Province, China (113°04' E, 28°11' N), from late June to late September 2020. The site is located in a semitropical monsoon climate area. The annual mean temperature is 17.2 °C, and the annual accumulated temperature is 5457 °C. The average annual precipitation is 1361.6 mm, which is mainly from April to October. The soil used in the study was deep soil (depth > 100 cm). The texture of soil is clay. The parent material of soil is fluvial deposits. The basic chemical properties of the test soil show that the soil pH was 5.43, total N was 0.85 g kg⁻¹; total P was 0.31 g kg⁻¹, total K was 14.39 g kg⁻¹, Alkaline N was 51.44 mg kg⁻¹, available P was 6.75 mg kg⁻¹, available K was 165.24 mg kg⁻¹, organic matter was 8.50 g kg⁻¹.

Ammonium sulfate, ammonium bisphosphate and potassium (K) chloride were applied as N, phosphorus (P) and K fertilizers. The rate of N fertilizer varied with treatment

while the amount of P and K fertilizer was 150 kg P_2O_5 ha⁻¹ and 200 kg K_2O ha⁻¹ for all treatments. The rice variety is mega rice. The growth period is 92 days.

2.2. Experimental Design

The fertilizer balls were prepared by mixing the fertilizers and red soil: clay ratio of 2:1, making fertilizer balls with a diameter of 1~1.5 cm, the fertilizer balls involved N, P and K mixed clay. The balled fertilizers were dried in a 30 °C oven for approximately two days. Fertilizer balls were applied between two rice lines by an injector [32]. The content of N, P, and K fertilizer was 10.59% (N), 3.31% (P_2O_5), and 8.82% (K_2O) for large granular fertilizer.

The pot experiment was carried out in plastic containers of length 42 cm × breadth 31.5 cm × depth 22.5 cm. There were seven treatments showed in Table 1. Each treatment had twelve replicates, and each stage had three replicates. Plastic film and a bird-proof net were used to protect the experiments from precipitation and birds.

Table 1. Fertilization treatments.

Treatment	Fertilizer Types	Fertilizer Depths	Nitrogen Application Rate
N ₀	--	--	--
S300	surface application	0 cm	300 kg N ha ⁻¹
S210	surface application	0 cm	210 kg N ha ⁻¹
R5	row application	5 cm	210 kg N ha ⁻¹
R10	row application	10 cm	210 kg N ha ⁻¹
B5	deep application	5 cm	210 kg N ha ⁻¹
B10	deep application	10 cm	210 kg N ha ⁻¹

Rice was transplanted on 22 June 2020 (seedlings of 21 days old). Four rice seedlings were planted in each container, arranging in two pairs. The planting density was 15 cm × 15 cm (Figure 1). For treatments S300 and S210, 75% N fertilizer was applied as base fertilizer, and 25% was applied as topdressing at tillering stage. Fertilizers in deep fertilization treatments were applied twice, before and after rice transplanting. Nitrogen and P were applied before transplanting the rice seedlings. The application rate is 60 kg N ha⁻² and 75 kg P_2O_5 ha⁻², respectively. For other treatments, base fertilizer was applied once by deep fertilization after rice transplanting. For the row application method, soil was first excavated a 5 cm or 10 cm depth ditch. Fertilizers were then spread evenly. Between the two lines, and the ditch was finally covered by soil. Rice in all pots were harvest on September 21, 2020. A 5 cm of water layer was maintained during the rice growing season.

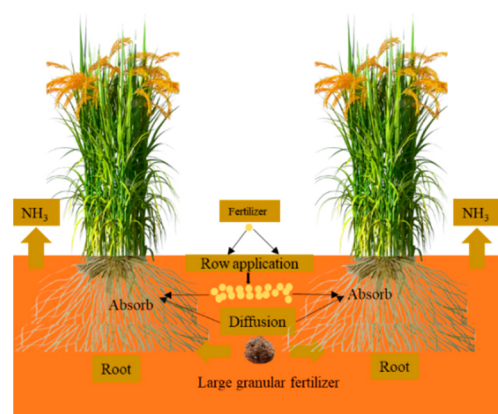


Figure 1. Schematic diagram of potted plants.

2.3. Sample Collection and Analysis

2.3.1. Soil Chemical Properties

Soil total nitrogen content was weighed and measured by the Kjeldahl apparatus after the air-dried soil samples with 100 mesh sieve holes were digested with mixed accelerator and H_2SO_4 . The contents of total phosphorus and total potassium in soil were measured by visible spectrophotometer and flame spectrophotometer after adding H_2SO_4 and HClO_4 to dry soil samples with 100 mesh sieve pores. Soil available phosphorus content was measured by visible spectrophotometer after adding phosphorus-free activated carbon and 50 mL $0.5 \text{ mol L}^{-1} \text{ NaHCO}_3$ to air-dried soil samples with 20 mesh sieve holes. The content of available potassium in soil was measured by flame photometer after adding 50 mL $1 \text{ mol L}^{-1} \text{ NH}_4\text{OAc}$ to the air-dried soil samples with 20 mesh sieve holes. In the determination of soil alkaline nitrogen, air-dried soil samples with 20 mesh sieve holes were weighed and determined by the alkaline hydrolysis diffusion method. Soil organic matter weighed 100 mesh sieve air-dried soil samples, adding $\text{K}_2\text{Cr}_2\text{O}_7\text{-H}_2\text{SO}_4$ solution after cooking, using $0.2 \text{ mol L}^{-1} \text{ FeSO}_4$ solution titration.

2.3.2. Dry Biomass and Grain Yield

During the growing season, rice samples (4 plants) were taken at tillering (13 July), full heading (23 August), filling (6 September), and maturity stage (21 September), respectively. The samples were washed with distilled water and divided into roots, stems, leaves, and panicles. We harvested three pots in each period, after removing plants from the soil, and slowly washed them with water until the root was thoroughly emerged. All plant samples, including the rice grain at maturity, were treated at 105°C for 30 min and then oven-dried at 65°C till constant weights.

2.3.3. Soil Nitrogen Transfer and Transformation

Stainless steel frames were used for soil sampling at the tillering, full heading, filling, and maturity stages (Figure 2). Centering on the fertilizer point, the frame had a length of 15 cm, a width of 5 cm, and a depth of 20 cm. The soil was later cut into small cubes of 2.5 cm length. Two soil cubes at equal distances on both sides of the fertilizer point were pooled as one sample. Soil $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$ were extracted from 5.00 g fresh soil samples, by 50 mL $2 \text{ mol L}^{-1} \text{ KCl}$. Then the sample was placed in constant temperature water bath with a constant temperature, 25°C , speed at 220 rpm, for 30 min of vibration time to determine the total N in soil extract right after extraction by continuous Flow Analyzer.



Figure 2. Soil sampling tool (a,b).

2.3.4. Determination of NH₃ Volatilization in Rice Field

In this experiment, NH₃ volatilization was measured by closed chamber extraction. The closed chamber was cylindrical organic glass (with an inner diameter of 14 cm and a height of 15 cm). When determining ammonia volatilization, 100 mL of 0.05 mol L⁻¹ H₂SO₄ was used as ammonia absorption liquid, and a flow meter was used to set the air exchange rate of 15–20 times the chamber size per minute [33]. The daily pumping time is morning (9:00–11:00) and afternoon (15:00–17:00), and 4 h represents the daily NH₃ volatile flux.

Ammonia volatilization was monitored after the first fertilization until no significant differences between fertilized treatments and the control. The collected ammonia volatile absorbent was analyzed using an AA3 flow analyzer.

2.3.5. Determination of NH₄⁺-N Concentration in Surface Water

While monitoring ammonia volatilization, we collected surface water to determine NH₄⁺-N concentration. It was determined by 0.45 µm membrane extraction with an AA3 flow analyzer.

2.4. Data Analysis

Calculation of Ammonia Volatilization

The ammonia volatilization was calculated using the following equation:

$$F = \frac{C \times V \times 6 \times 10^{-6}}{\pi \times r^2 \times 10^{-4}}$$

where F means the NH₃ emission flux (kg ha⁻¹ d⁻¹); C means NH₄⁺-N concentration in the absorber; V means the dilute sulfuric acid absorbs liquid volume (L); the 6 represents conversion to one-day emission flux; the 10⁻⁶ represents mg conversion to kg; r is the radius of the closed chamber collecting ammonia volatilization; 10⁻⁴ represents m² conversion to ha.

The loss rate of ammonia volatilization was calculated by the equation below:

$$R = (F_W - F_0)/f$$

where R represents loss rate of ammonia volatilization (%); F_W represents the cumulative Flux of NH₃ Emission in N region (kg ha⁻¹ d⁻¹); F₀ represents the cumulative Flux of NH₃ Emission in Non-nitrogen Application region (kg ha⁻¹ d⁻¹); f represents fertilizer N application (kg ha⁻¹).

The calculation formulas of nitrogen recovery efficiency (NRE) and nitrogen agroeconomic efficiency (NAE) are as follows:

$$NRE = (N - N_0)/F$$

$$NAE = (GY - GY_0)/F$$

where N means the N uptake of aboveground parts of plants under N application, N₀ is the N uptake of aboveground parts of plants without N application, GY is the dry biomass of grain under N application, GY₀ represents the dry biomass of grain without N application, and F represents the N application amount of fertilizer.

The data were analyzed through analysis of variance (ANOVA) using the SPSS18.0 (Norman H. Nie, C. Hadlai (Tex) Hull and Dale H. Bent; SPSS; American) software. The statistical differences between treatment means were determined by the least significant difference (LSD) (*p* < 0.05).

3. Results

3.1. Effects of Fertilization on Dry Biomass Quality and Yield of Plants

3.1.1. Dynamics of Rice Dry Biomass

During the growth season, the root biomass of different fertilization treatments varied significantly. Under the traditional application of nitrogen fertilizer, the S300 treatment increased by 12.74% and 7.36% respectively compared with the S210 treatment at the filling and maturity stage. At the same fertilization depth, the root biomass of the B5 treatment increased by approximately 1.0% compared with that in the R5 treatment during filling and maturity stage. The root biomass of the B10 treatment increased by 2.2% and 1.4% at both stages, compared with those of the R10 treatment. The root biomass of deep application of 10 cm (B10, R10) increased by 4.69–5.93% and 3.36–3.22%, respectively, compared with deep application of 5 cm (B5, R5) at the filling and mature stage. In addition, root biomass in B10 increased by 0.9% compared with conventional N treatment at maturity.

In general, shoot showed significant differences between treatments, as well as the total biomass of rice. The shoot biomass and total biomass of S300 treatment were 14.56%, 11.83%, 17.48%, 28.53%, and 21.34%, 11.73%, 18.60%, 20.48% higher than those of S210 treatment in the tillering, full heading, filling and maturity stage, respectively, indicating that in the soil with low fertility, reducing the amount of nitrogen fertilizer by 30% under scattered fertilization would affect the growth of rice. At the same fertilization depth, the shoot dry biomass and total dry biomass of B5 treatment were respectively 1.6%, 0.8%, 5.3%, 6.7%, and 7.5%, 1.1%, 2.1%, 4.7% higher than those of R5 treatment at tillering, full heading, filling and maturity stage. The shoot dry biomass and total dry biomass of B10 were 11.9%, 3.3%, 6.7%, 5.9%, and 7.1%, 3.1%, 5.2%, 4.3% higher than those of R10 treatment at tillering, full heading, filling and maturity stage, separately. The dry biomass of deep application of 5 cm (B5, R5) was lower than those of deep application of 10 cm (B10, R10), indicating that plant nutrient absorption was mainly concentrated in the vicinity of 10 cm below the root, which promoted the absorption of nutrient and affected rice yield (Table 2).

Table 2. Dry biomass of medium rice at different growth stages under different fertilization methods.

Growth Period	Treatment	Dry Biomass (g Plot ⁻¹)					
		Leaf	Stem and Sheath	Panicle	Root	Shoot	Shoot + Root
Tillering	S300	17.82 ± 0.36	22.14 ± 0.40 ^b	-	19.74 ± 0.72 ^a	39.96 ± 0.75 ^b	59.70 ± 1.15 ^a
	S210	16.98 ± 0.48	17.90 ± 0.04 ^d	-	14.31 ± 0.09 ^c	34.88 ± 0.45 ^c	49.20 ± 0.36 ^c
	R5	16.33 ± 1.27	19.79 ± 0.25 ^c	-	15.63 ± 0.50 ^b	36.12 ± 1.46 ^c	51.75 ± 1.74 ^c
	R10	17.47 ± 0.13	21.94 ± 0.48 ^b	-	17.11 ± 0.41 ^b	39.41 ± 0.35 ^b	56.52 ± 0.52 ^b
	B5	16.69 ± 1.05	20.02 ± 0.37 ^c	-	18.91 ± 0.39 ^a	36.71 ± 0.90 ^c	55.62 ± 1.05 ^b
	B10	17.62 ± 0.32	26.46 ± 0.58 ^a	-	16.45 ± 0.69 ^b	44.08 ± 0.83 ^a	60.53 ± 0.14 ^a
		$p = 0.678$	$p < 0.05$		$p < 0.05$	$p < 0.05$	$p < 0.05$
Full heading	S300	65.21 ± 2.05 ^a	185.70 ± 1.55 ^a	39.02 ± 0.52 ^a	87.96 ± 0.27	288.08 ± 7.36 ^a	376.04 ± 7.10 ^a
	S210	58.19 ± 1.22 ^b	166.14 ± 1.49 ^b	33.28 ± 0.50 ^b	78.94 ± 2.64	257.61 ± 0.84 ^b	336.55 ± 2.96 ^b
	R5	59.27 ± 0.46 ^{ab}	180.07 ± 0.97 ^a	35.13 ± 0.35 ^b	80.90 ± 6.38	274.47 ± 1.04 ^{ab}	355.37 ± 7.42 ^{ab}
	R10	61.67 ± 3.15 ^a	183.85 ± 5.76 ^a	36.90 ± 1.88 ^a	84.91 ± 1.88	284.43 ± 6.04 ^a	367.34 ± 4.18 ^a
	B5	61.14 ± 0.20 ^a	180.09 ± 1.83 ^a	35.50 ± 0.88 ^{ab}	82.62 ± 3.34	276.72 ± 1.71 ^{ab}	359.34 ± 4.86 ^{ab}
	B10	66.27 ± 2.13 ^a	186.41 ± 3.24 ^a	39.12 ± 0.26 ^a	86.86 ± 1.88	291.80 ± 4.26 ^a	378.66 ± 3.66 ^a
		$p = 0.054$	$p < 0.05$	$p < 0.05$	$p = 0.403$	$p < 0.05$	$p < 0.05$
Filling	S300	61.20 ± 0.26 ^a	174.19 ± 2.16 ^a	81.40 ± 0.41 ^a	152.68 ± 0.38 ^a	316.79 ± 2.07 ^a	469.47 ± 2.24 ^a
	S210	44.16 ± 0.49 ^c	153.30 ± 0.45 ^d	63.94 ± 0.65 ^c	135.43 ± 1.03 ^c	261.40 ± 0.20 ^e	395.83 ± 1.20 ^e
	R5	45.59 ± 1.80 ^c	164.97 ± 1.56 ^c	70.32 ± 0.42 ^b	144.48 ± 0.58 ^b	273.77 ± 3.19 ^d	425.36 ± 1.39 ^d
	R10	54.37 ± 0.86 ^b	174.80 ± 1.60 ^a	70.80 ± 0.23 ^b	151.25 ± 0.66 ^a	299.97 ± 0.96 ^b	451.22 ± 1.45 ^b
	B5	52.72 ± 0.47 ^b	157.86 ± 1.36 ^b	70.63 ± 0.06 ^b	145.91 ± 1.96 ^b	288.33 ± 1.98 ^c	434.23 ± 2.65 ^c
	B10	61.49 ± 0.75 ^a	175.99 ± 0.40 ^a	82.46 ± 1.90 ^a	154.56 ± 1.69 ^a	319.93 ± 2.07 ^a	474.49 ± 3.72 ^a
		$p < 0.05$	$p < 0.05$	$p < 0.05$	$p < 0.05$	$p < 0.05$	$p < 0.05$
Maturity	S300	57.36 ± 0.55 ^a	171.23 ± 0.29 ^a	101.01 ± 0.75 ^a	168.90 ± 1.45 ^a	329.60 ± 1.34 ^a	498.49 ± 1.60 ^a
	S210	38.91 ± 1.56 ^d	147.79 ± 2.17 ^{cd}	69.73 ± 4.81 ^d	157.32 ± 2.73 ^c	256.43 ± 5.43 ^d	413.75 ± 6.21 ^d

R5	45.54 ± 0.19 ^c	152.15 ± 1.54 ^c	84.13 ± 2.22 ^c	162.87 ± 1.75 ^b	281.83 ± 2.45 ^c	444.70 ± 4.01 ^c
R10	52.19 ± 0.39 ^b	167.49 ± 2.28 ^b	96.51 ± 1.80 ^a	168.11 ± 1.15 ^a	316.19 ± 3.11 ^b	484.30 ± 1.97 ^b
B5	49.92 ± 0.59 ^c	156.21 ± 2.31 ^c	94.53 ± 2.41 ^{ab}	164.87 ± 1.44 ^{ab}	300.37 ± 3.55 ^c	465.53 ± 2.95 ^c
B10	57.89 ± 0.64 ^a	173.88 ± 0.82 ^a	103.07 ± 2.00 ^a	170.41 ± 1.13 ^a	334.83 ± 2.55 ^a	505.25 ± 1.45 ^a
	$p < 0.05$	$p < 0.05$	$p < 0.05$	$p < 0.05$	$p < 0.05$	$p < 0.05$

Different letters within each column of a growth stage indicate the treatments differ at the $p < 0.05$ statistical significance level (Mean ± SE, $n = 3$).

3.1.2. Rice Grain Yield, NRE, and NAE

Among the fertilization treatments, the yield of the B10 treatment was similar to that of the S300 treatment. Compared with S210 treatment, deep application treatment (R5, R10, B5, B10) increased yield by 20.98%, 41.75%, 39.63%, 56.37%, respectively (Table 3). At the same fertilization depth, the yield of the B5 treatment was 15.42% higher than that of the R5 treatment. The yield of the B10 treatment was 10.32% higher than that of the R10 treatment.

Table 3. Effects of different fertilization methods on grain yield and N use efficiency.

Treatment	N Uptake of Aboveground Parts of Plants	NRE	NAE	Grain Yield
	g Plot ⁻¹	%	kg kg ⁻¹	t ha ⁻¹
S300	4.42 ± 0.03 ^a	24.66 ± 0.19 ^d	4.94 ± 0.53 ^c	32.47 ± 2.56 ^a
S210	3.22 ± 0.12 ^d	23.26 ± 1.14 ^d	3.65 ± 0.47 ^d	20.93 ± 1.58 ^b
R5	3.64 ± 0.01 ^c	27.46 ± 0.14 ^c	4.95 ± 0.94 ^c	25.32 ± 3.19 ^b
R10	4.07 ± 0.03 ^b	31.77 ± 0.26 ^b	6.23 ± 0.17 ^{ab}	29.67 ± 0.56 ^a
B5	3.92 ± 0.09 ^b	30.22 ± 0.91 ^b	6.10 ± 0.62 ^b	29.23 ± 2.11 ^{ab}
B10	4.44 ± 0.07 ^a	35.42 ± 0.65 ^a	7.14 ± 1.09 ^a	32.73 ± 3.69 ^a
N ₀	0.87 ± 0.01 ^e	-	-	8.56 ± 0.12 ^c
	$p < 0.05$	$p < 0.05$	$p < 0.05$	$p < 0.05$

Different letters within each column mean treatments differ at the $p < 0.05$ statistical significance level (Mean ± SE, $n = 3$).

As compared with S300, while reducing N fertilizer by 30%, NRE of deep application increased by 18.07–52.28%. When compared to the S210 treatment, the NAE of deep application increased by 35.62–95.62%. Among them, the B10 treatment showed the highest NRE. At the same fertilization depth, the NRE and the NAE of the B5 treatment increased by 10.05% and 23.23% respectively, compared with the R5 treatment. The NRE and NAE of B10 treatment were 11.49% and 14.61% higher than those of the R10 treatment, respectively. The results showed that deep application helped N uptake of rice plants, reducing N loss and improving N utilization efficiency.

3.2. Diffusion Dynamics of Soil NH₄⁺-N and NO₃⁻-N by Fertilization Method

3.2.1. Vertical and Horizontal Distribution of Soil NH₄⁺-N

Effects of fertilization on NH₄⁺-N distribution in soil are shown in Figure 3. For the conventional N fertilizer treatments (S300, S210), the NH₄⁺-N is mainly distributed on the soil surface, and the concentration in the top soil is higher than that in the bottom soil. The NH₄⁺-N concentrations of S300 were ranged in 144.51–255.19 mg kg⁻¹, 149.01–183.96 mg kg⁻¹, 71.05–87.54 mg kg⁻¹, 34.90–55.02 mg kg⁻¹; S210 NH₄⁺-N concentrations ranged from 144.33–196.34 mg kg⁻¹, 136.23–186.25 mg kg⁻¹, 47.63–68.38 mg kg⁻¹, 22.66–43.54 mg kg⁻¹ at the tillering, full heading, filling and maturity stage. For deep treatment, all fertilization depths (5 cm, 10 cm) in soil showed the highest concentration of NH₄⁺-N, formed the center of fertilization, and gradually spread to the surrounding soil. The soil NH₄⁺-N concentration under large granular fertilizer deep application was mainly concentrated in the horizontal direction 5–7.5 cm, the vertical direction 3–15 cm soil layer, around the rice root system, slowed down the diffusion rate of the NH₄⁺-N, and then ensured the sufficient

nutrient supply during the rice growth period. However, the distribution of soil $\text{NH}_4^+\text{-N}$ concentration in different fertilization depths was different under the row deep application. The $\text{NH}_4^+\text{-N}$ concentrated in the horizontal direction of 0–5 cm and the vertical direction of 3–9 cm soil area under the deep application of 5 cm, the soil $\text{NH}_4^+\text{-N}$ mainly concentrated in the horizontal direction of 3–7.5 cm, the vertical direction of 3–15 cm soil layer under the depth of 10 cm.

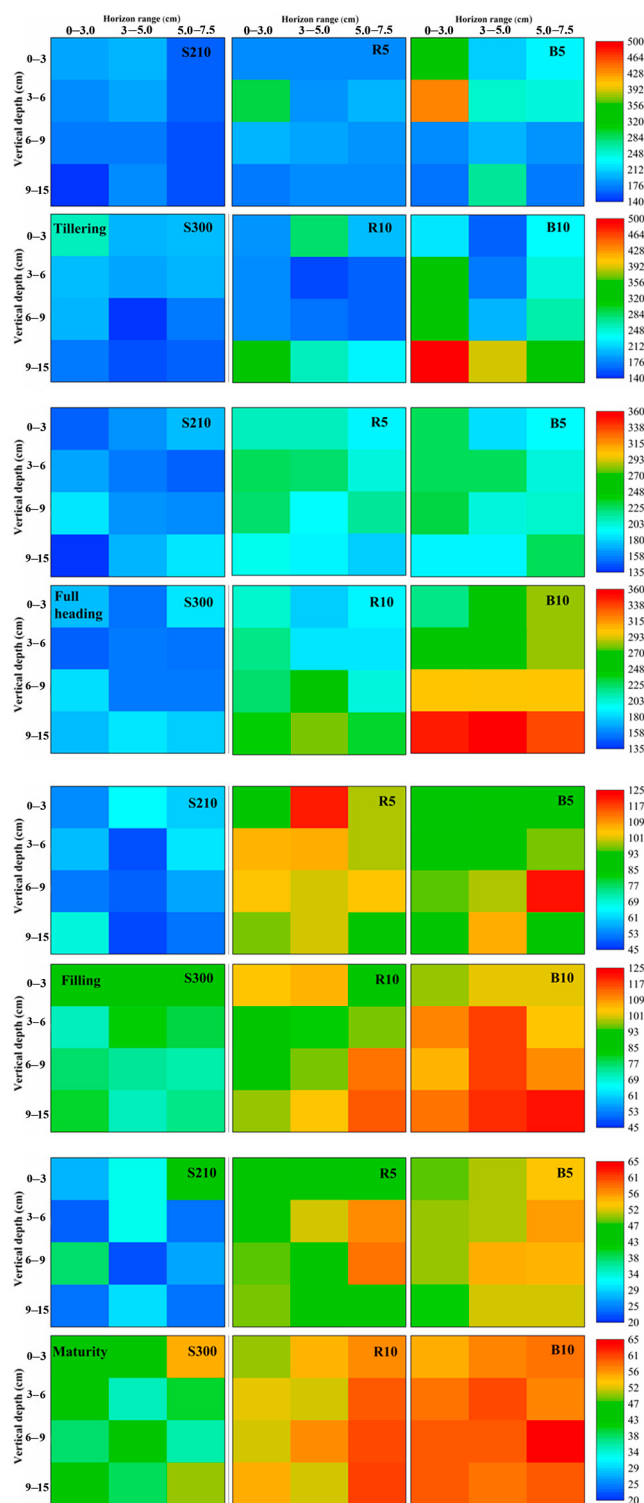


Figure 3. $\text{NH}_4^+\text{-N}$ content in different soil layers at tillering stage, full heading stage, filling stage and maturity stage (mg/kg).

For deep treatment, the maximum soil $\text{NH}_4^+\text{-N}$ concentration all appeared at tillering stage. At the same fertilization depth, $\text{NH}_4^+\text{-N}$ at 5 cm depth concentrated in a 3–6 cm depth (vertical), 0–3 cm (horizontal) soil area, showing its highest concentration, R5 treatment was $292.96 \text{ mg kg}^{-1}$, B5 treatment was $437.54 \text{ mg kg}^{-1}$. The $\text{NH}_4^+\text{-N}$ in depth of 10 cm existed in a 9–15 cm depth (vertical) and 0–3 cm (horizontal) soil area, and the highest concentration R5 treatment was $317.82 \text{ mg kg}^{-1}$, B10 treatment was $496.31 \text{ mg kg}^{-1}$. During the growth period, the soil $\text{NH}_4^+\text{-N}$ content decreased. After maturity, the $\text{NH}_4^+\text{-N}$ concentration range of R5 treatment was $44.07\text{--}57.97 \text{ mg kg}^{-1}$, and that of B5 treatment was $47.82\text{--}55.53 \text{ mg kg}^{-1}$. The $\text{NH}_4^+\text{-N}$ concentration range of the R10 treatment was $49.71\text{--}61.10 \text{ mg kg}^{-1}$, and that of the B10 treatment was $55.17\text{--}64.34 \text{ mg kg}^{-1}$. The concentration of $\text{NH}_4^+\text{-N}$ in the 5 cm soil layer was concentrated in a 3–9 cm vertical direction and 3–7.5 cm horizontal direction. $\text{NH}_4^+\text{-N}$ concentration in 10 cm deep soil was finally concentrated in 3–15 cm in the vertical direction and 3–7.5 cm in the horizontal direction. Therefore, when the fertilization depth is 10 cm, the soil $\text{NH}_4^+\text{-N}$ content has been maintained at a high level, so that the nutrients of rice will not be lost quickly during the growth process, the nutrient utilization ratio of the plant will be improved, and the plant will grow better.

3.2.2. Vertical and Horizontal Distribution of Soil $\text{NO}_3^-\text{-N}$

As shown in Figure 4, at the tillering stage, the traditional nitrogen fertilizer application treatment was mainly on the soil surface (0–3 cm), the concentration of $\text{NO}_3^-\text{-N}$ was $10.93\text{--}43.72 \text{ mg kg}^{-1}$; the deep application treatment was mainly inside the soil at fertilization sites (3–15 cm), the concentration of $\text{NO}_3^-\text{-N}$ was $5.98\text{--}32.48 \text{ mg kg}^{-1}$. The $\text{NO}_3^-\text{-N}$ concentration of conventional N fertilizer was significantly higher than those of deep application. The concentrations of $\text{NO}_3^-\text{-N}$ at full heading, filling, and maturity stage under the conventional N fertilizer application were $4.3\text{--}19.77 \text{ mg kg}^{-1}$, $8.82\text{--}11.64 \text{ mg kg}^{-1}$ and $7.49\text{--}10.52 \text{ mg kg}^{-1}$, respectively. The $\text{NO}_3^-\text{-N}$ concentrations at full heading, filling and maturity stage were $2.32\text{--}17.90 \text{ mg kg}^{-1}$, $7.38\text{--}10.25 \text{ mg kg}^{-1}$ and $4.70\text{--}9.00 \text{ mg kg}^{-1}$, respectively, under the deep application of large granular fertilizer. The $\text{NO}_3^-\text{-N}$ concentrations at full heading, filling and maturity stage were $6.91\text{--}19.46 \text{ mg kg}^{-1}$, $8.37\text{--}12.40 \text{ mg kg}^{-1}$ and $5.29\text{--}7.05 \text{ mg kg}^{-1}$, respectively, under the treatment of deep row application. The $\text{NH}_4^+\text{-N}$ concentration of inorganic N in soil is mainly $\text{NH}_4^+\text{-N}$, $\text{NO}_3^-\text{-N}$ relatively low. As well, the effects of fertilization on soil $\text{NO}_3^-\text{-N}$ concentration in different treatments were similar. Therefore, the $\text{NH}_4^+\text{-N}$ in fertilizer is rarely converted to $\text{NO}_3^-\text{-N}$.

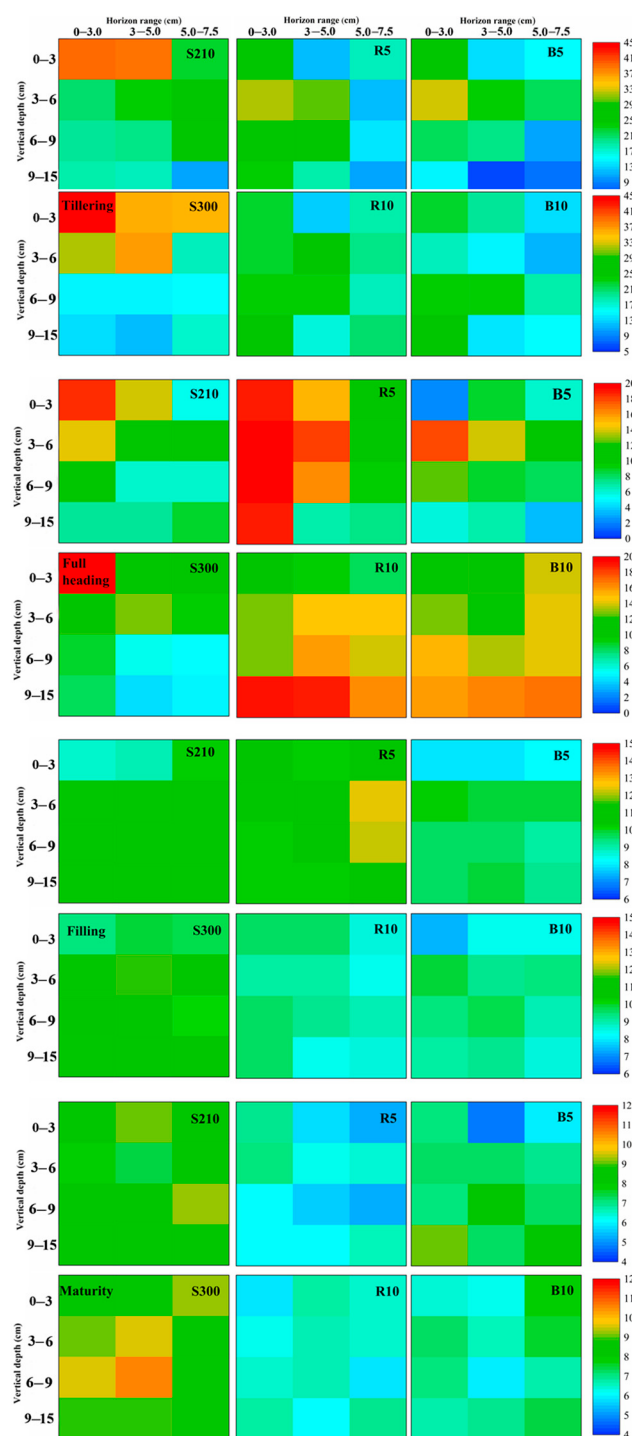


Figure 4. $\text{NO}_3\text{-N}$ content in different soil layers at tillering stage, full heading stage, filling stage and maturity stage (mg/kg).

3.3. Effects of Fertilization Methods on Ammonia Volatilization in Paddy Field

3.3.1. Dynamics of Ammonia Volatilization Flux

Ammonia volatilization peak of each fertilization treatment appeared on the first day after the application of base fertilizer (Figure 5). The volatilization rate of S300 treatment was $8.67 \text{ kg ha}^{-1} \text{ d}^{-1}$, while that of B10 was only $3.05 \text{ kg ha}^{-1} \text{ d}^{-1}$. The peak value of the S210 treatment is 41.18% lower than that of the S300 treatment. Moreover, the peak value of

other deep application treatments (R5, R10, B5) was 58.71–63.32% lower than that of the S300 treatment. At the same fertilization depth, the peak value of ammonia volatilization flux of B5 treatment was similar to that of R5, while the peak value of ammonia volatilization flux in B10 treatment was 4.1% lower than that in R10 treatment.

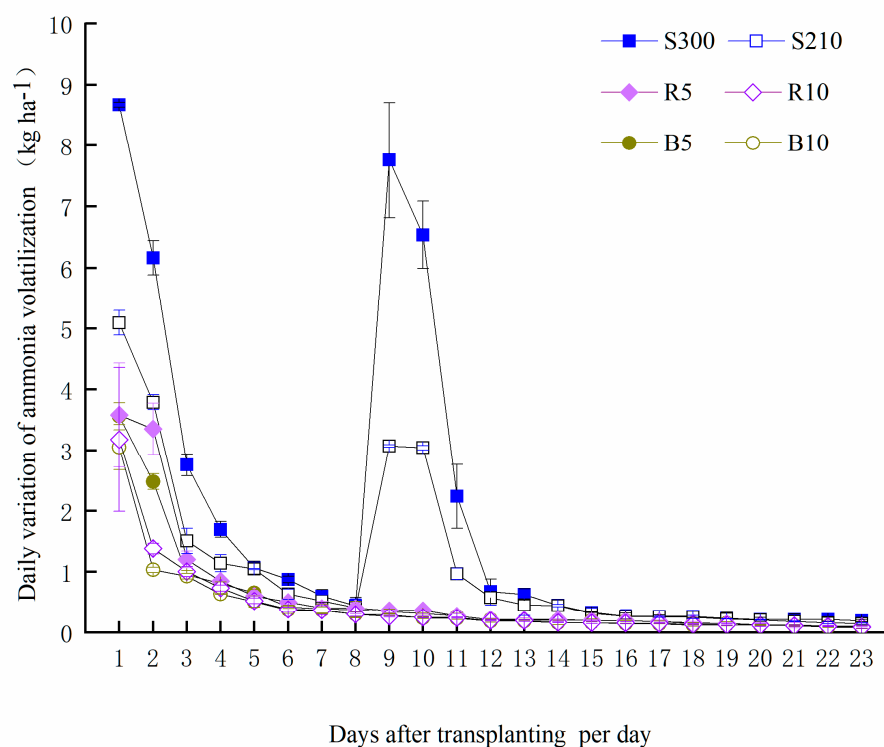


Figure 5. Daily variation of ammonia volatilization in different fertilization treatments.

On the 9th day after topdressing, the second ammonia volatilization peak appeared in the conventional fertilizer treatments. At this time, the ammonia volatilization amounts of S300 and S210 treatments were $7.76 \text{ kg ha}^{-1} \text{ d}^{-1}$ and $3.07 \text{ kg ha}^{-1} \text{ d}^{-1}$, respectively, which were both lower than each of their first peaks, due to the low N application of tillering fertilizer. There were no second peaks in other treatments due to the lack of topdressing. Subsequently, ammonia volatilization of each fertilization treatment showed a downward trend, until the 23rd day after fertilization, ammonia volatilization of each fertilization treatment and no fertilization treatment (N_0) were not significantly different.

3.3.2. Ammonia Volatilization Loss and Loss Rate

During the monitoring period of ammonia volatilization in rice fields (in total of 23 days), the ammonia volatilization loss and ammonia volatilization loss rate of the conventional N fertilizer spread treatment were the highest, ammonia volatilization loss was 42.76 kg ha^{-1} and 24.70 kg ha^{-1} , respectively. Ammonia volatilization loss rate was 12.30% and 9.0% respectively (Table 4). The cumulative ammonia volatilization loss of the N_0 treatment was the lowest, and the cumulative ammonia volatilization loss of the B10 treatment was at a very low level in the fertilization treatment, and there was a significant difference among the fertilization treatments. The cumulative loss of ammonia volatilization ranked as $S300 > S210 > R5 > B5 > R10 > B10$, and the cumulative loss of ammonia volatilization of B10 was significantly lower than all other fertilized treatments.

Table 4. Ammonia volatilization loss and ammonia volatilization loss rate with different fertilization methods.

Treatment	Nitrogen Application	Total Ammonia Volatilization	Ammonia Volatilization Loss Rate
	kg ha ⁻¹	kg ha ⁻¹	%
N ₀	0	5.85 ± 2.00 ^g	—
S300	300	42.76 ± 1.20 ^a	12.3
S210	210	24.70 ± 0.15 ^b	9.0
R5	210	13.84 ± 1.27 ^c	3.8
R10	210	10.30 ± 1.16 ^e	2.1
B5	210	12.47 ± 0.30 ^d	3.2
B10	210	9.57 ± 0.55 ^f	1.8

Different letters for total ammonia volatilization indicate treatments are different at the $p < 0.05$ statistical significance level (Mean ± SE, $n = 3$).

Deep application of N fertilizer reduction can significantly reduce ammonia volatilization loss, the ammonia volatilization loss rates of row deep application (R5, R10) were 3.80% and 2.12%, respectively, which were 69.10% and 82.76% lower than those of S300 treatment, respectively. The ammonia volatilization loss rates of deep application of large granular fertilizer (B5, B10) were 3.15% and 1.77%, respectively, which were 74.39% and 85.63% lower than those of S300 treatment, respectively. At the same fertilization depth, the ammonia volatilization loss rate of the B5 treatment was 17.19% lower than that of the R5 treatment. The ammonia volatilization loss rate of the B10 treatment was 16.64% lower than that of the R10 treatment. Therefore, the deeper the fertilization depth was, the lower the ammonia volatilization loss (rate) was. Under the same fertilization depth, the fertilization method of deep application of large granular fertilizer had the best effect on inhibiting ammonia volatilization loss. The above results showed that fertilization methods had a significant effect on ammonia volatilization loss. Deep application treatment could effectively reduce ammonia volatilization. As well, applying fertilizer at 10 cm depth was better than at 5 cm depth, which was better than surface application.

3.3.3. NH₄⁺-N Concentration in Surface Water

The concentration of NH₄⁺-N in surface water after fertilization was basically consistent with that of ammonia volatilization (Figure 6). The highest NH₄⁺-N concentration in surface water appeared on the first day after fertilization, and then gradually decreased. The NH₄⁺-N concentration of S300 treatment was 275.84 mg L⁻¹ on the first day after the application of base fertilizer. The concentration of B10 was 118.73 mg L⁻¹. Compared with the S300 treatment, the peak of NH₄⁺-N concentration decreased by 26.0–57.0% after deep fertilization. Under the same fertilization depth, the peak NH₄⁺-N concentration of the B5 treatment was 17.3% lower than the R5 treatment, and the B10 treatment was 10.68% lower than the R10 treatment. After topdressing, the peak value of NH₄⁺-N concentration in the S300 treatment was the highest, which was 128.28 mg L⁻¹. Compared with the S300 treatment, the peak value of NH₄⁺-N concentration in deep topdressing treatment decreased by 56.4–72.5%. At the same fertilization depth, the NH₄⁺-N concentration peak of the B5 treatment was 7.39% lower than that of the R5 treatment. B10 treatment decreased by 15.8% compared with the R10 treatment. There was no significant difference among the treatments after 23 days. The NH₄⁺-N concentration in surface water of fertilization treatment was generally S300 > S210 > R5 > B5 > R10 > B10.

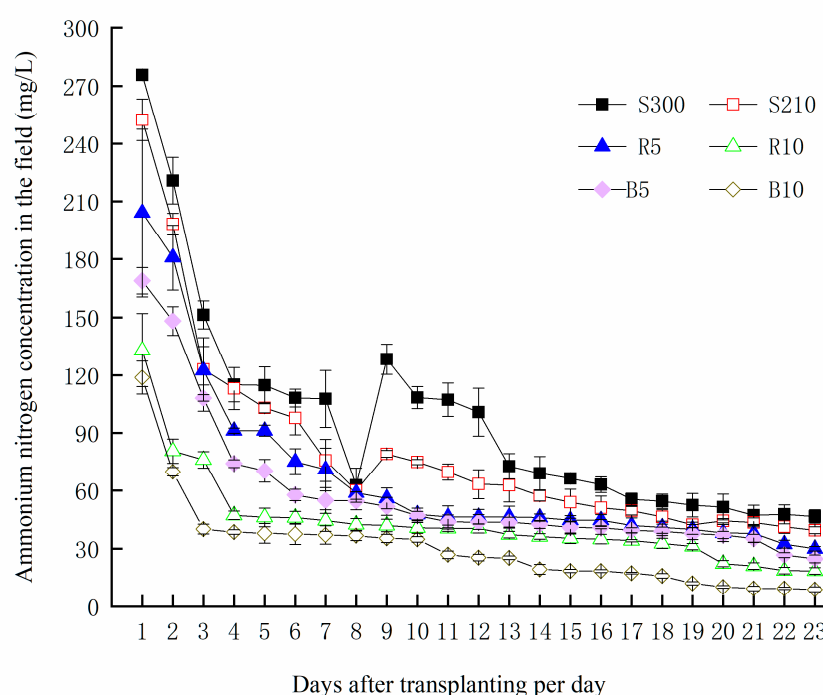


Figure 6. Daily variation of ammonium nitrogen concentration in surface water under different fertilization treatments.

4. Discussion

4.1. Effects of Fertilization on Soil N Distribution

The release and migration of N fertilizer in soil affected the absorption and utilization of N in rice. Previous studies showed that the soil depth of the paddy field is mainly in an anaerobic environment. Soil inorganic N is maintained as of $\text{NH}_4^+\text{-N}$. Deep fertilization increases the contact between particles and soil, and reduces the loss of N through runoff and other forms [33–35]. In this study, the soil $\text{NH}_4^+\text{-N}$ concentration under deep application was significantly higher than that under conventional N application, and the soil $\text{NH}_4^+\text{-N}$ was mainly concentrated in 6–15 cm. Rice roots were mainly distributed in the 0–20 cm tillage layer [36,37]. The deep application of fertilizer over 7.5 cm obtained the maximum N availability, promoting the increase of nutrient concentration in the crop root zone, making rice fully absorb nutrients, and improving crop yield. This is why 5 cm and 10 cm depth were used as the fertilization depth under deep fertilization.

In addition, N distribution occurred mainly in the 0–5 cm soil layer [38], showing that $\text{NH}_4^+\text{-N}$ diffusion rate was very slow in root zone fertilization mode, which could be maintained for about 2 months, and the diffusion range was only 4–13 cm below the soil surface [18]. The results of this study showed that deep fertilization could gradually migrate and spread around the fertilization point. Comparing the changes of $\text{NH}_4^+\text{-N}$ concentration in different deep fertilization methods, the distribution of fertilizer N in the horizontal direction is 5–7.5 cm under the large granular deep fertilization. As well, the vertical direction distribution is mainly in the soil layer ranging from 3–15 cm. The migration distance of fertilizer N under the deep application varies by fertilization depth. The distribution of fertilizer N in the horizontal direction was 0–5 cm under the deep application of 5 cm, which was mainly distributed in the range of 3–9 cm in the vertical direction. The migration distance of fertilizer N in the horizontal direction was 3–7.5 cm under the deep application of 10 cm, while was mainly distributed in the range of 3–15 cm in the vertical direction. The results of the studies of Wu, etc., are similar [39]. The main reason may be that the fertilizer is loose and not concentrated enough compared with large granular ferti-

zation, resulting in soil $\text{NH}_4^+\text{-N}$ loss. Previous studies have shown that in the 60-day period of rice cultivation, the conventional N fertilizer application resulted in high $\text{NH}_4^+\text{-N}$ content in the soil surface, while the deep application significantly increased the $\text{NH}_4^+\text{-N}$ content around the fertilization point (the depth of deep application was 10 cm), and the duration was long [40,41]. This is consistent with the results of this study. In this study, the soil $\text{NH}_4^+\text{-N}$ concentration under the deep application treatment was still high until the mature stage, which could ensure the continuous nutrient supply of plants in the growth period. However, the soil $\text{NH}_4^+\text{-N}$ concentration under the conventional N fertilizer application treatment decreased due to excessive N loss. Since the effects of fertilization treatments on the vertical and horizontal migration of $\text{NO}_3^-\text{-N}$ in paddy soil were not significant in this study, it was not discussed.

4.2. Effect of Fertilization on Ammonia Volatility in Paddy Field

Previous studies showed that $\text{NH}_4^+\text{-N}$ was buried under the soil surface layer by deep application, which reduced the loss of NH_3 volatilization [34,41]. Our results also showed that deep N application significantly reduced the cumulative NH_3 loss in rice growing season, and the loss rate of ammonia volatilization was only 1.8%–3.8%, and the deeper the depth was, the lower the loss rate of ammonia volatilization was. On the one hand, the reason is that deep application will make the $\text{NH}_4^+\text{-N}$ concentration in the soil last for a long period, slow down the hydrolysis rate of fertilizer, and then reduce the NH_3 volatilization loss. Secondly, deep application increased the adsorption of $\text{NH}_4^+\text{-N}$ on the soil exchange complex with a negative charge, which could reduce the $\text{NH}_4^+\text{-N}$ concentration in surface water, thereby reducing the NH_3 volatilization loss [34,42]. The results showed that the loss rate of ammonia volatilization was lower than that of Shang *et al.* [43]. The main reason was that the N fertilizer used in this experiment was ammonium sulfate, which was the fertilizer to inhibit the loss of ammonia volatilization. In this study, under the same fertilization depth, ammonia volatilization loss of deep application of large granular fertilizer was significantly lower than that of row application. The result is similar to that of Ke *et al.* [17]. The reason may be the difference in fertilization shape. Large granular fertilizer act as a package., when fertilizer is applied, the film can hinder the loss of N; the row application release so fast that $\text{NH}_4^+\text{-N}$ cannot stay the in soil for long period. Therefore, the above phenomenon further shows that reducing the $\text{NH}_4^+\text{-N}$ concentration in the surface water is the reasonable way to reduce NH_3 volatilization in the paddy field.

$\text{NH}_4^+\text{-N}$ mainly exists in the form of ionic ammonia and non-ionic ammonia, and non-ionic nitrogen (NH_3) is one of the important factors affecting the growth of aquatic animals (fish, crustaceans) [44]. In the ecological agriculture mode, in addition to farmland fertilization, aquatic animals also have the excretion of ammonia-containing products [45]. When the non-ionic ammonia in surface water increases, hemoglobin loses the function of carrying oxygen, reduces the oxygen-carrying capacity and energy metabolism of aquatic animals, inhibits the ammonia excretion of aquatic animals, and causes a series of physiological toxicity reactions such as hypoxia and organ failure and death [46,47]. The results of this study showed that deep application could significantly reduce the $\text{NH}_4^+\text{-N}$ concentration in surface water and ensure the normal growth of aquatic organisms due to the deep burial of fertilizers in the soil layer and the reduction of volatilization in air.

4.3. Effects of Fertilization on Rice Growth

The essence of rice yield formation is the accumulation, transfer, and distribution of dry biomass [48]. Different from the previous experiments, the sub-surface soil of rice fields with relatively poor fertility was used in this experiment, and the experimental results are sensitive to the differences between different fertilization treatments. The N uptake of rice at the early growth stage was limited [24]. However, at the full heading stage, most N fertilizers were gradually absorbed. The accumulation and transfer of N at the full heading stage is a critical period for grain yield, since most of the dry biomass in leaves and stem sheaths are transferred to grains during this period, and 70% of the N absorbed

by straw is transferred to grains in the meantime, which will keep the N accumulation in grains at a certain level during plant maturation [49]. As well, roots penetrating more than 20 cm into the soil, still can absorb nutrients from the soil [50]. In this study, compared with the conventional N fertilizer application, the dry biomass of deep application at the tillering stage was low, while the dry biomass showed an increasing trend after the heading stage, for the roots are mainly distributed in the shallow layer in the early stage. However, at the full heading stage, the root development gradually completes. The observation is comparable with the results from previous results [51,52]. Some research showed that the NRE of deep application increased by 30–54 %, and grain yield was significantly increased, compared with the conventional N fertilizer application [34,53]. Deep application increased the number of effective tillers in the early growth stage, and significantly increased the number of effective panicles and yield at maturity [39]. This study showed that the deep application of B10 significantly increased the dry biomass of each part of the rice plant and yield. The main reason can be that deep application gives the possibility for the rice roots to fully contact with fertilizer, provides high nutrient concentration to promote rice tillering, enhances root activity and increases yield during rice growth and development; [54] reported similar results. It is reported that deep fertilization does not lead to yield decline with a reduction in the application rate of N fertilizer by 28–44% [22].

Moreover, the results of this study showed that under the same fertilization depth, the rice yield under the treatment of the deep application of large granular fertilizer increased by 10.32–15.42% compared with that under the treatment of row deep fertilization. Under the same fertilization mode, the rice yield of deep application of 10 cm was higher than that of deep application of 5 cm. On the one hand, the row treatment fertilizer is loose, the fertilizer was released in the soil fast, and there was limited nutrient for the rice during the critical period of growth; on the other hand, the fertilization depth may not be enough for the loss of some nutrients in rice growth [34,37] studies showed that, NRE and grain yield had no correlation with fertilization depth. In this study, deep application significantly increased NRE and NAE. Although the N₀ treatment contained less N in our study, it was close to the atmospheric N deposition content and could be ignored. Grain yield was lowest at 20 cm, followed by deep 5 cm, Deep application of 10 cm is the best [37]. The main reason may be that N loss processes (such as nitrification and denitrification) differ in different soil depths [55].

5. Conclusions

Deep application can effectively inhibit ammonia volatilization and reduce N loss. Compared with conventional fertilization, deep application reduces the number of top-dressing and can improve farmers' production efficiency. According to the migration characteristics of N in soil during the growth period of rice, deep application of large granular fertilizer promotes the growth of rice. It not only makes the fertilizer have full contact with the rice root system, but also provides sufficient nutrients for the vegetative growth stage of rice and slows down the release rate of N. The large granular fertilizer fertilization technology is worth exploring and developing, but the technology requires large labor costs. Therefore, it is necessary to further develop and promote large granular fertilization technology and fertilization equipment to reduce the production costs.

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