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Long-Term Straw Return with Reducing Chemical Fertilizers Application Improves Soil Nitrogen Mineralization in a Double Rice-Cropping System

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Abstract: The partial replacement of chemical fertilizer with straw return is considered an effective method for improving the accumulation of organic matter and soil fertility, but the characteristics of soil nitrogen fixation and mineralization in a double-cropped rice paddy system are unclear. Based on a 12-year field experiment, we conducted a waterlogged incubation experiment for 49 days to determine the effect of long-term straw return combined with reducing chemical fertilizer application on the dynamic changes of mineralized soil nitrogen (N) content and mineralized N rate under the treatments, including NPK (chemical fertilizers application with straw removal), SBR (straw burned return), and SR (straw return). Results showed that, compared with SBR and NPK, SR significantly increased available nitrogen by 7.4% and 16.5%, respectively, due to the higher ammonium nitrogen and nitrate nitrogen, as well as the total carbon, available phosphorus, and slowly available potassium, suggesting that it could stock a sufficient nitrogen source. During the incubation period, the amount of N mineralization was relatively higher under SR than under SBR and NPK treatments, especially during the later mineralization time, whereas there was no difference in the N mineralization rate. In addition, SR significantly increased soil cumulative N mineralization and N mineralization potential. However, SBR significantly decreased the soil mineralizable N ratio compared with SR and NPK, which may result in a worsening of the N mineralization potential. The results indicated that long-term straw return combined with reducing chemical fertilizer application could significantly improve the N supply capacity of paddy rice field soil to better coordinate the soil N supply and immobilization.

Keywords: long-term straw return experiment; double-cropped rice paddy system; substitution of partial chemical fertilizer; nitrogen mineralization

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1. Introduction

Nitrogen (N) is the most important nutrient that limits the productivity of agroecosystems, and more than 90% of the nitrogen in soil is in the form of organic nitrogen [1]. Only a small part of water-soluble organic nitrogen in soil can be absorbed and utilized by plants directly, and most organic nitrogen can be absorbed and utilized by plants only after mineralization. Soil organic nitrogen mineralization provides available nitrogen for plants, which determines the soil nitrogen supply capacity to a great extent [2]. Factors such as crop residue management, fertilizer application system, and fertilizer and soil characteristics affect the microbial biomass and activity as well as microbial community structure and functioning [3], which, in turn, affects the process of soil organic nitrogen mineralization and its mineralization capacity. In particular, different residue retention practices result in significant changes in the properties and environmental conditions of paddy soils, which may affect the mineralization capacity of soil organic nitrogen [4]. Therefore, it is important to deepen the understanding of soil organic nitrogen mineralization to optimize the soil nitrogen supply in the paddy rice agroecosystem and prevent environmental nitrogen loss.

In farmland ecosystems, fertilization is a common measure for regulating the nitrogen supply of farmland soil and the nitrogen nutrition of crops [5]. Increasing nitrogen fertilizer can enhance the net nitrogen mineralization rate of soil nitrogen, but excessive nitrogen fertilizer will inhibit the mineralization of soil organic nitrogen [6]. Long-term excessive fertilization leads to constraints on increased crop yields, soil fertility, and the rate of nitrogen transformation in paddy fields. It is recognized that the combined application of nitrogen fertilizer and organic matter (such as crop residue and livestock manure) is considered one of the most sustainable and economical methods to coordinate the nitrogen supply and rice production and sustainable agricultural practices to replenish soil nitrogen stocks [7,8]. Generally, crop residue retention can increase the organic nitrogen content of the soil by more than 70%, especially dissolved organic nitrogen [9]. Straw returning promotes the mineralization and decomposition of native soil organic matter to form soluble organic nitrogen [10]. Meanwhile, straw contains various organic compounds, some of which can be converted into small molecules of soluble organic nitrogen during mineralization and decomposition [7]. In addition, the partial replacement of chemical fertilizer with in situ crop residue retention demonstrates significantly increased content of soluble organic nitrogen and microbial nitrogen in soil, as well as the unstable nitrogen pool, and enhances the mineralization process of nitrogen transformation, providing inorganic nitrogen sources for plant growth [11,12]. However, rice straw burning has always existed in rice production, especially in multi-season rice rotation areas, such as the double-cropping system. Thus, it is particularly necessary to compare the advantages and disadvantages of returning rice straw to the field and rice straw burning to determine the feasibility of returning rice straw to the field based on the efficient supply of soil nutrients.

Flooded incubation, proposed by Warning et al. [13], was suggested as an extremely important biological method to study soil nitrogen mineralization. This method can better simulate the water status of flooded soil, and it does not need to consider aeration and strict water control in the incubation process, so it is widely used in the study of nitrogen mineralization in paddy soil [14]. Submergence incubation creates conditions that are suitable for organic nitrogen mineralization and inhibits the activity of nitrifying bacteria. The final product of mineralization is ammonium nitrogen, and there is no volatilization loss under airtight conditions [15]. Short-term incubation (around 2 months) of soil was suggested as a simpler, faster, and more practical method for N mineralization [16]. More importantly, the nitrogen released by submerged incubation can not only represent the nitrogen released from flooded paddy soil but also reflect the nitrogen uptake of crops.

Many studies have reported that the effects of reduced inorganic fertilizer application with in situ actual crop residue retention on rice yields [17], N fertilizer efficiency [18], and soil fertility [19] had positive effects. However, little information exists regarding the effects of long-term straw application on the soil nitrogen mineralization in a double rice-cropping system in subtropical China. Thus, the aim of the present study was to improve the understanding of N mineralization in response to different rice straw practices under equal nutrient application that have been applied to the experimental site for the past 12 years.

2. Materials and Methods

2.1. Field Site

The long-term straw returned double-cropping rice field experiment was conducted at the National Soil Fertility Monitoring (NSFM) site, located in Yangxi Village, Wenzhen Town, Jinxian County, Jiangxi Province, China (28°20′7.14″ N, 116°5′29.73″ E). The area has a subtropical monsoon climate. The annual precipitation is 1600–1800 mm. The annual frost-free period is 291 d. The average annual sunshine duration is 1900.5 h, and the average annual temperature is 17.5 °C. The paddy soils of the site are Quaternary red clay developed paddy soils with moderate soil fertility. The soil properties are 5.48 pH, 19.8 g kg^{-1} total carbon, 2.27 g kg^{-1} total nitrogen, 126.0 mg kg^{-1} alkaline hydrolysable-N, 31.4 mg kg^{-1} available phosphorus, and 97.9 mg kg^{-1} available potassium contents.

2.2. Experimental Design and Soil Collection

Details of the long-term field experimental design, chemical fertilizer application, and nutrient content of straw and straw ash have been described in Huang et al. [20] and in Table 1. In brief, 4 treatments with 3 replications (comprising 12 plots) were established in 2010 as follows in the field experiments. (1) CK, no chemical fertilizers application with straw removal as control; (2) NPK, chemical fertilizers application with straw removal; (3) SBR, straw burned return with reducing chemical fertilizers; (4) SR, straw return with reducing chemical fertilizers. After the early and late rice harvests of each season, rice straw and straw ash were returned to the field in situ as the base fertilizer for the next season, respectively. The weight of rice straw (straw ash) input to the farmland per season was calculated based on a grain to straw ratio of 1:1 and a straw burning factor of 85.72%. The nutrient content was calculated based on the results of its dry sample measurement and the final converted straw input to the farmland. The three fertilization treatments had the equal N, P, and K nutrients input, and any insufficient nutrient content of N, P, and K from straw and straw ash was supplemented by chemical fertilizers (containing N, P_2O_5, and K_2O). The total application amount of nitrogen, phosphorus (P_2O_5), and potassium (K_2O) for early rice were 165, 75, and 150 kg ha^{-1}, and for late rice, they were 195, 87.75, and 175.5 kg ha^{-1}, respectively. The sources of inorganic N, P, and K fertilizers were urea, calcium magnesium phosphate, and potassium chloride, respectively.

Table 1. Nutrient input from chemical fertilizers and organic manure (straw or straw ash) in treatments (kg ha^{-1}).

Season	Treatment	N		P_2O_5		K_2O	
		Fertilizer	Organic Manure	Fertilizer	Organic Manure	Fertilizer	Organic Manure
Early rice	CK	0	0	0	0	0	0
	NPK	165.00	0	75.00	0	150.00	0
	SBR	163.00	2.00	73.00	2.00	77.00	73.00
	SR	116.40	48.60	72.00	3.00	75.00	75.00
Late rice	CK	0	0	0	0	0	0
	NPK	195.00	0	87.80	0	175.50	0
	SBR	193.06	1.94	81.00	6.80	60.00	115.50
	SR	143.00	52.00	78.80	9.00	63.00	112.50

CK: no chemical fertilizers application with straw removal; NPK: chemical fertilizers application with straw removal; SBR: straw burned return with reducing chemical fertilizers; SR: straw return with reducing chemical fertilizers.

Soil samples were taken to 0.2 m depths from 5 points randomly selected within each plot after the rice harvests on 25 October 2021. All samples were naturally air-dried and sieved through a 2 mm screen. The soil parameters, including total carbon, available nitrogen, ammonium nitrogen, nitrate nitrogen, available phosphorus, available potassium, and slowly available potassium of samples from each plot, were analyzed by following the method of Bao [21]. Total nitrogen was determined by the Kjeldahl method.

2.3. Soil Nitrogen Mineralization Determination

Soil N mineralization was carried out by constant temperature micro-incubation in airtight plastic jars under dark conditions without any added materials. Briefly, 10 g of soil was placed in 300 mL plastic jars in which 20 mL of distilled water was added and kept for 7 days under dark conditions to restart microbial activity. Each treatment had three replicates. After 7 days of pre-cultivation, the rubber cap was covered tightly and kept at a constant temperature of 25 °C. Samples were collected on the 7th, 14th, 21st, 28th, 35th, 42nd, and 49th d during the incubation period to determine the extractable ammonium nitrogen (NH_4^+-N). In brief, 50 mL 2 M KCl solutions were added to the fresh soil, then shaken at 200 rpm for 1 h, filtered with filter paper, and the NH_4^+-N content was measured using a Continuous Flow Analyzer (AA3, Bran + Luebbe, Hamburg, Germany).

N mineralization rate was calculated by the following equation [22,23]:

$$A_{amm} = C\ [NH_4^+-N]_{i+j} - C\ [NH_4^+-N]_i \quad (1)$$

$$R_{amm} = A_{amm}/\Delta d \quad (2)$$

$$\Delta d = d_{i+j} - d_i \quad (3)$$

where A_{amm} is the amount of NH_4^+-N mineralization in a certain incubation time (mg kg^{-1}); C $[NH_4^+-N]_i$ and C $[NH_4^+-N]_{i+j}$ are the contents of soil NH_4^+-N on day i and day i + j (mg kg^{-1}), respectively; R_{amm} is ammoniation rate (mg kg^{-1} d^{-1}); Δd is the sampling interval, day (d); d_i is the initial time of incubation, d_{i+j} is the end time of incubation.

The N mineralization potential and mineralization rate constants were calculated by the first-order reaction kinetic model formula:

$$N_d = N_0\ (1 - e^{-kd}) \quad (4)$$

where N_d is soil mineralization accumulation (mg kg^{-1}), and N_0 is N mineralization potential (mg kg^{-1}); *K* is the mineralization rate constant (d^{-1}); d is the incubation time (day). The parameters N_0 and *k* of the first-order reaction kinetic model of different treatments are obtained by fitting the measured data of ammonium nitrogen accumulation.

2.4. Statistical Analysis

Data were analyzed using SPSS 19.0 (SPSS Inc., Chicago, IL, USA), and the means of the treatments were examined by the Duncan test at $p = 0.05$ probability level.

3. Results

3.1. Soil Properties

Long-term straw return with reducing chemical fertilizers had positive effects on soil properties (Table 2). Compared to the NPK and SBR treatment, SR significantly increased the available nitrogen by 7.4% and 16.5%, respectively, which was associated with the highest ammonium nitrogen and nitrate nitrogen, with increases of 26.7~31.2% and 30.7~38.5%, respectively. The pH and total nitrogen under SR and SBR treatments were significantly higher than those under NPK and CK treatments. SR also significantly increased total carbon, available phosphorus, and slowly available potassium; however, SBR obtained the highest available potassium among the treatments.

Table 2. Soil physico-chemical properties under different long-term straw return treatments in double-cropping rice fields.

Treatment	pH	TC g kg^{-1}	TN g kg^{-1}	AN mg kg^{-1}	NH_4^+-N mg kg^{-1}	NO_3^--N mg kg^{-1}	AP mg kg^{-1}	AK mg kg^{-1}	SAK mg kg^{-1}
CK	5.25 ^{b}	21.49 ^{c}	2.29 ^{c}	208.81 ^{d}	9.13 ^{c}	0.16 ^{b}	5.52 ^{c}	43.63 ^{d}	163.66 ^{c}
NPK	5.20 ^{b}	24.74 ^{b}	2.59 ^{b}	233.30 ^{c}	16.02 ^{b}	0.18 ^{b}	16.12 ^{b}	96.28 ^{b}	201.73 ^{b}
SBR	5.43 ^{a}	25.00 ^{b}	2.91 ^{a}	252.90 ^{b}	17.06 ^{b}	0.16 ^{b}	17.92 ^{b}	109.01 ^{a}	211.82 ^{b}
SR	5.45 ^{a}	28.60 ^{a}	2.99 ^{a}	271.70 ^{a}	23.28 ^{a}	0.26 ^{a}	22.22 ^{a}	83.02 ^{c}	220.04 ^{a}

Means followed by different letters for the season are significantly different at $p < 0.05$ level. CK: no chemical fertilizers application with straw removal; NPK: chemical fertilizers application with straw removal; SBR: straw burned return with reducing chemical fertilizers; SR: straw return with reducing chemical fertilizers. TC: total carbon; TN: total nitrogen; AN: available nitrogen; NH_4^+-N: ammonium nitrogen; NO_3^--N: nitrate nitrogen; AP: available phosphorus; AK: available potassium; SAK: slowly available potassium.

3.2. Dynamics of Soil Nitrogen Mineralization

The process of soil nitrogen mineralization was essentially the same for all the treatments, and the accumulated mineralized nitrogen increased gradually with the prolongation of incubation time. (Figure 1). During the whole incubation process, the order of accumulated mineralized nitrogen content of each treatment from high to low is generally SR, SBR or NPK, and CK. On the 14th, 21st, 42nd, and 49th days of the incubation, the accumulated mineralized N in SR was higher than the other treatments, with the differences reaching significant levels.

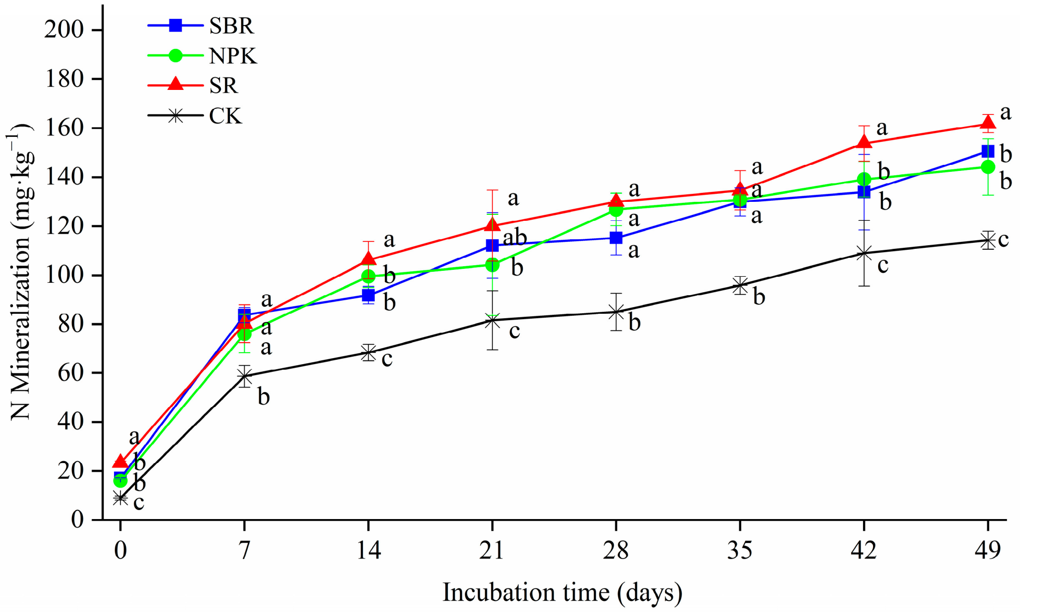

Figure 1. Dynamics of N mineralization of different long-term straw return modes. Different lowercase letters indicate significant differences ($p < 0.05$) among the treatments. CK: no chemical fertilizers application with straw removal; NPK: chemical fertilizers application with straw removal; SBR: straw burned return with reducing chemical fertilizers; SR: straw return with reducing chemical fertilizers.

The rate of soil nitrogen mineralization in each treatment gradually decreased as the incubation time increased and leveled off after the 28th day of incubation (Figure 2). The nitrogen mineralization rate of the three fertilization treatments was significantly higher than that of CK, but overall there was no significant difference between the three fertilization treatments. The nitrogen mineralization rate of SR was significantly higher than that of SBR on the 14th day of incubation.

3.3. Cumulative N Mineralization and N Mineralization Potential

The accumulated mineralized nitrogen content and potentially mineralizable nitrogen content of the three fertilization treatments on the 49th day were significantly higher than that of the CK treatment (Figure 3). Among the fertilization treatments, the accumulated mineralized nitrogen content and potentially mineralizable nitrogen content under SR were significantly higher than that of SBR and NPK. However, there were no significant differences in cumulative mineralized nitrogen content and potentially mineralizable nitrogen content between SBR and NPK, and cumulative mineralized nitrogen was lower under NPK, though with no difference.

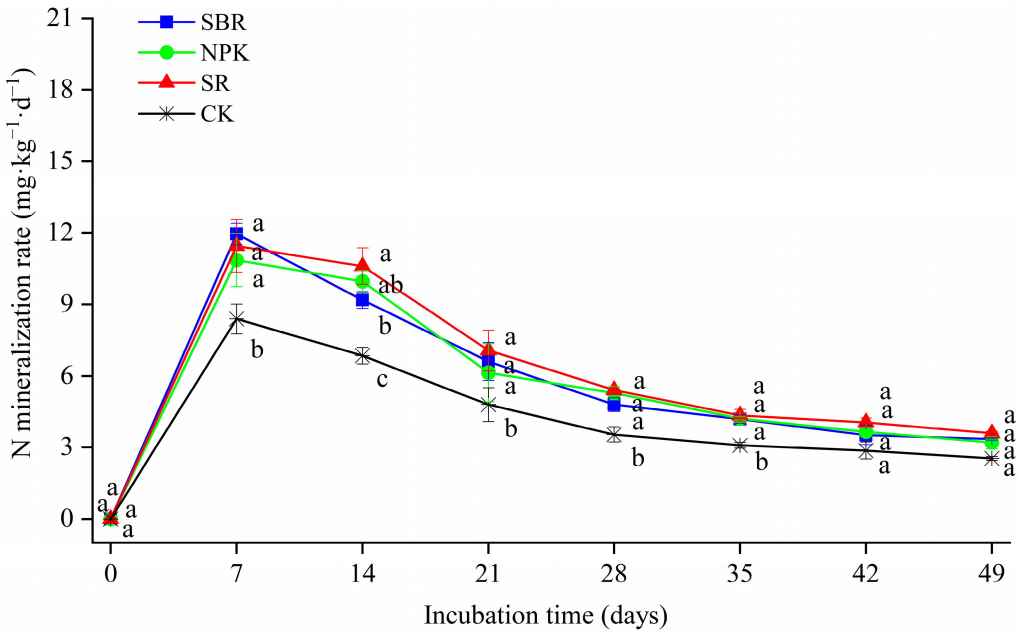

Figure 2. Dynamics of N mineralization rate of different long-term straw return modes. Different lowercase letters indicate significant differences (p < 0.05) among the treatments. CK: no chemical fertilizers application with straw removal; NPK: chemical fertilizers application with straw removal; SBR: straw burned return with reducing chemical fertilizers; SR: straw return with reducing chemical fertilizers.

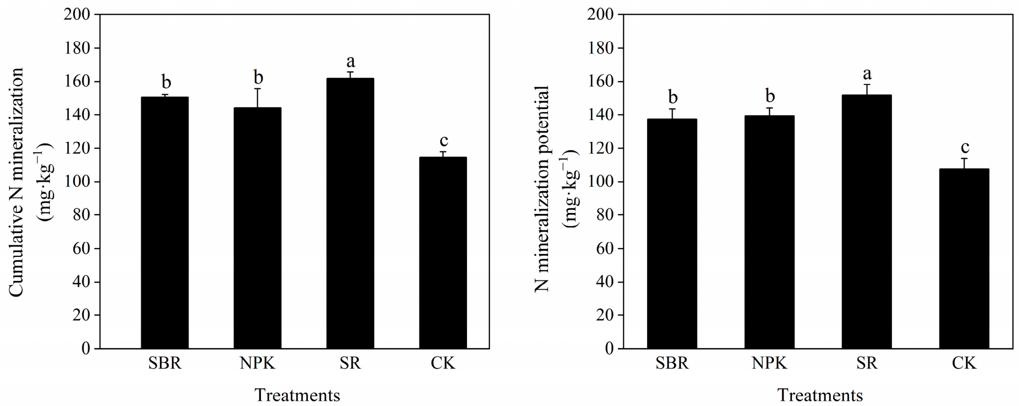

Figure 3. Cumulative N mineralization and N mineralization potential of different long-term straw return modes. Different lowercase letters indicate significant differences (p < 0.05) among the treatments. CK: no chemical fertilizers application with straw removal; NPK: chemical fertilizers application with straw removal; SBR: straw burned return with reducing chemical fertilizers; SR: straw return with reducing chemical fertilizers.

3.4. Kinetic Characteristics of Soil Nitrogen Mineralization

A single-order exponential equation was used to fit the process of soil nitrogen mineralization, and good results were obtained that R^2 was 0.871~0.922 with $p < 0.05$ (Table 3). Compared with CK, three fertilization treatments significantly increased the k value. Both SR and NPK treatment significantly increased the soil mineralizable nitrogen ratio by 0.54 and 0.53 percentage points, respectively, compared with SBR, and the soil mineralizable nitrogen ratio of SBR was the same as that of CK.

Table 3. Values of parameters obtained from fitting of the first-order reaction dynamic model in fitting test at different straw return treatments.

Treatment	Mineralization Rate Constant *k* mg kg^{-1} d^{-1}	Determination Coefficients R^2	Mineralizable Nitrogen Ratio %
CK	0.09 [a]	0.871 *	4.99 [b]
NPK	0.11 [a]	0.922 *	5.56 [a]
SBR	0.11 [a]	0.858 *	5.03 [b]
SR	0.10 [a]	0.900 *	5.57 [a]

Means followed by different letters for the season significantly different at $p < 0.05$ level. * Denotes significant correlation at $p < 0.05$. CK: no chemical fertilizers application with straw removal; NPK: chemical fertilizers application with straw removal; SBR: straw burned return with reducing chemical fertilizers; SR: straw return with reducing chemical fertilizers.

4. Discussion

4.1. Effects of Long-Term Straw Return on Soil Fertility Quality

Rice straw contains a large number of rich mineral nutrients, which will inevitably increase the enrichment of soil surface nutrients after returning straw to the field and plays an important role in improving soil nitrogen, phosphorus, and potassium nutrients [24,25]. Studies have shown that returning straw to the field can increase soil organic matter, and improve soil fertility, thereby contributing to sustainable rice production [26]. Our results showed that, compared with the beginning of the experiment, the soil nutrient content increased in varying degrees after 12 years of long-term fertilization and straw returning to the field. SR treatment was beneficial in increasing the content of soil organic carbon, alkali-hydrolyzable nitrogen, NH_4^+-N, NO_3^--N, and available phosphorus, suggesting that stock soil N supply was sufficient. Lower pH may be the reason for the low content of available nitrogen in CK and NPK treatments. It showed that returning straw to the field based on reducing the application of chemical fertilizer was of great significance to the improvement of soil fertility. The decomposed straw provides rich nutrients such as carbon, nitrogen, phosphorus, and potassium for the soil, and the increased organic matter promotes the activity of soil microorganisms and enzymes, which releases a large number of nutrients and enhances their effectiveness [26–28]. However, the burning of straw had no significant effect on soil fertility since straw burning wasted a lot of biomass energy and nutrients, resulting in the loss of major nutrients and emitting a lot of pollutants [29,30]. During open-burning of rice straw in the field, some N and S may be lost due to volatilization, and nutrients in organic matter are rapidly converted into inorganic N, P, K, Ca, and Mg, which can be rapidly lost by leaching and erosion [31]. Repeated burning in the field results in a permanent reduction in total biological activity, in which the bacterial population permanently diminishes by more than 50% [32].

Additionally, the content of available soil potassium in SR treatment was significantly lower than that of SBR and NPK, which may be attributed to the absorption of the above-ground plant, whereas the content of slowly available potassium was the opposite trend. The reasons may be due to the fact that organic acids such as oxalic acid, citric acid, tartaric acid, and malic acid produced by rice straw decomposition can promote the release of mineral potassium, thus increasing the content of slowly available potassium in soil [33]. In summary, our results suggested that the use of straw returning to replace some chemical fertilizers promoted the sustainable development of double-cropping rice production.

4.2. Effects of Long-Term Straw Return on Nitrogen Mineralization

In rice production, about 50% and 80% of the nitrogen absorbed by rice comes from soil [34]. As the main component of soil nitrogen, only some small molecular organic nitrogen can be directly absorbed and utilized by crops [35,36]. However, most organic nitrogen must be converted into inorganic nitrogen by mineralization before it can be directly absorbed and utilized by crops [37]. Therefore, the storage of soil organic nitrogen and its mineralization ability plays an important role in rice's high yield and nitrogen-efficient utilization. The process of soil nitrogen mineralization is affected by soil organic matter and total nitrogen content [38]. We found that long-term fertilization, especially straw replacement of part of chemical fertilizer, significantly increased soil cumulative mineralized nitrogen and mineralizable nitrogen ratio, which were consistent with the results of previous studies [18,25]. This was mainly related to the fact that returning straw to the field replenishes a large amount of organic matter in the soil in the form of organic fertilizer, indicating that the application of straw can obviously enhance the mineralization of soil nitrogen and increase the content of soil active organic nitrogen. Long-term straw returning to the field instead of partial fertilization can simultaneously increase the soil nitrogen supply capacity and improve the nitrogen quality, while the soil substrate quality without organic matter decreases, weakening its nitrogen supply capacity to a certain extent. This explanation is consistent with Govaerts et al. [39], who reported that long-term burning straw significantly reduced the potentially mineralizable N. The microbial community and organic matter decreased immediately after burning straw, even hindering weed growth, further reducing the input of organic matter into the soil.

Nitrogen mineralization potential is the maximum amount of organic nitrogen that can be mineralized to inorganic nitrogen in soil under certain conditions, which characterizes the potential of soil nitrogen supply. In this study, we found a high level of N mineralization potential and mineral N content in the SR field soil (Figure 3), which indicated that continuous straw replacement significantly enhances the nitrogen supply capacity of soil. Crop residues are the major source of organic nitrogen for decomposers, which, in turn, produce inorganic nitrogen and control the long-term availability of soil nitrogen [4]. Plant residues and root exudates provide a continuous source of active nitrogen to maintain microbial growth and stimulate mineralization [40]. In our study, the long-term application of rice straw in situ to replace part of chemical fertilizer had the best effect in increasing the supply capacity of soil mineralization nitrogen and improving the supply characteristics of soil nitrogen. This should be related to the comprehensive effects of many factors, such as the application of organic fertilizer directly supplying a large amount of active nitrogen to the soil compared with straw burning and the single application of chemical fertilizer, which can better enhance the microbial activity and increase the amount of nitrogen returned to the field of rice stubble. Furthermore, the temperature is an important environmental factor affecting soil nitrogen cycling processes, and the environmental temperature patterns of straw returning to the field of early rice and late rice are quite different. Hence, the temperature sensitivity of nitrogen mineralization characteristics of double-cropping paddy soil under different straw returning methods needs to be further studied.

5. Conclusions

After 12 years of soil management, our study found that long-term straw return management and fertilization had great influences on N sequestration and N mineralization. Long-term partial replacement of chemical fertilizer with in situ crop residues could significantly improve soil N sequestration and soil TN storage, mainly attributed to the improvements in TN, AN, NH_4^+-N, and NO_3^--N. During the incubation time, the amount of N mineralization was significantly higher under SR in terms of the highest soil cumulative N mineralization and its potential, indicating that the soil nitrogen supply of SR was relatively more rapid and sustained. These results suggested that long-term straw return with reducing chemical fertilizers not only improved the nutrient stocks and soil fertility but also enhanced nitrogen supply capacity in double-season rice fields.

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