



## Study on the Effect of Water, Fertilizer and Biochar Interaction on N<sub>2</sub>O Emission Reduction in Paddy Fields of Northeast China

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### ABSTRACT

Taking the black soil of northeastern cold land as the research object, this paper adopts the three-factor quadratic saturation D311 optimal design scheme, uses static black box-gas chromatography to analyse the irrigation season, nitrogen fertilizer and straw biochar to the impact of greenhouse gas emissions for N<sub>2</sub>O growing season in the northeast cold paddy field. This paper also studies the optimal water and fertilizer application scheme for N<sub>2</sub>O control. The results show that the effects of three factors on N<sub>2</sub>O emissions are as follows: nitrogen fertilizer > biochar > water. The irrigation and biochar have an inhibitory effect on N<sub>2</sub>O emissions, while nitrogen fertilizer has a promoting effect on N<sub>2</sub>O emissions. The performance is as follows: water + nitrogen fertilizer can promote the emission of N<sub>2</sub>O; water + biochar can inhibit the emission of N<sub>2</sub>O; nitrogen fertilizer + biochar can promote the emission of N<sub>2</sub>O. Combined with the yield, the integrated water and biochar optimization schemes, when controlling the increase of N<sub>2</sub>O growth season in paddy fields to not exceed 10% are as follows: The amount of irrigation is 4252~5531 kg/hm<sup>2</sup>; the nitrogen application rate is 103.30~117.35 kg/hm<sup>2</sup>; and the amount of biochar is 15.12~24.42 t/hm<sup>2</sup>.

### INTRODUCTION

Northeastern China is an important production base of national commercial grain in China. The paddy field in Northeast China has increased rapidly in the past decade, and paddy fields are the main source of agricultural greenhouse gas emissions, which plays a significant role in the global greenhouse effect (Bouwman et al. 2002). As a trace greenhouse gas, N<sub>2</sub>O contributes about 7.9% to the greenhouse effect (IPCC 2007). Relevant research shows that about 80% of China's current total N<sub>2</sub>O emissions have derived from agricultural emissions (Ghosh et al. 2003). According to statistics, on a 100 year timescale, the global warming potential of N<sub>2</sub>O is 298 times that of CO<sub>2</sub> (Zhang et al. 2011). Therefore, the research on N<sub>2</sub>O emission patterns and growth season emissions of paddy fields in the northeastern cold land has a positive significance for mitigating greenhouse gas emissions and proposing emission reduction measures.

There are many factors affecting the N<sub>2</sub>O emission in paddy fields. Studies show that when the irrigation amount is sufficient, the N<sub>2</sub>O emissions are rare when the paddy fields are flooded for a long time, and the N<sub>2</sub>O emissions

will account for more than 85% of the total entire growth period of the rice when the surface has no water layer (Xu et al. 2000). The excessive wet and dry alternating water will significantly increase the N<sub>2</sub>O emissions (Zhou et al. 2013). Some scholars believe that (Kang et al. 2013), frequent water layer changes and baking technology can increase N<sub>2</sub>O emissions significantly in rice fields. But because the paddy field water control period is often in the period of strong crop growth, soil nitrogen content is not high, so the increase of N<sub>2</sub>O emissions is also at a low level, the overall impact from the global warming potential (GWP) is not significant. Fertilization measure is one of the factors affecting N<sub>2</sub>O emissions in rice fields, which can be artificially controlled. Some studies have pointed out that the application of nitrogen fertilizer is the main factor for N<sub>2</sub>O emissions from farmland mineral soils (Meng et al. 2005). According to the EIA survey, 78% of N<sub>2</sub>O emitted from agricultural soils in the United States has derived from the application of nitrogen fertilizer (EIA 2005). Wang et al. (2003) showed that the amount of chemical fertilizer applied was reduced to 50% and 0; N<sub>2</sub>O emissions from soil were reduced by 22% and 41% of current emissions, respectively.

As an important recycling resource, people have paid attention to biochar because it has a carbon sequestration effect on soil and can reduce greenhouse gas emissions. Zhang et al. (2012) found that under the application of nitrogen fertilizer, the application of biochar can inhibit the  $N_2O$  emission of rice fields by 66%, the effect of 40 t/hm<sup>2</sup> carbon treatment is better, and the sustained effect is longer. Cayuela et al. (2014) believe that biochar significantly reduces the total  $N_2O$  emissions. Shenbagavalli & Mahimairaja (2012) found that biochar could inhibit the release of greenhouse gases, of which  $CO_2$  and  $N_2O$  are most effective.

At present, although many scholars have carried out related research on the effects of water, fertilizer and biochar on the  $N_2O$  emissions from paddy fields, they are basically studied by single factors, and most of them are concentrated in the paddy fields in the south (Shi et al. 2011, Yuan et al. 2008, Liang et al. 2004, Knoblauch et al. 2008, Qin et al. 2015). The impact of its integrated management on  $CH_4$  emission patterns in rice fields (factor coupling effects) has rarely reported, and research on northeast rice fields is less involved. The purpose of this experiment is to analyse the coupling effect of three factors of water, nitrogen fertilizer, and biochar on greenhouse gas emissions, and to combine the  $N_2O$  emission reduction targets in the paddy field to find the optimal water, fertilizer, and biochar-blending scheme. In the end, this paper provides a field management technique that can be used for the reduction of  $N_2O$  in the paddy field in the northeastern cold land.

## MATERIALS AND METHODS

**Overview of the test site:** The experiment was carried out from May to October 2017 at the Rice Irrigation Test Center Station (125°44'E, 45°63'N) in Heping Town, Qing'an County, Heilongjiang Province. It is a typical cold soil black soil area. The average annual temperature is 2.5 °C, the average annual precipitation is 550 mm, and the average annual water surface evaporation is 750 mm. The water-heat growth period of crop is 156 to 171 days, and the annual frost-free period is 128 days. The climate is characterized by a cold temperate continental monsoon climate. The soil type is a white type of paddy soil with a bulk density of 1.01 g/cm<sup>3</sup> and a porosity of 61.8%. The basic physical and chemical properties of the soil include organic matter mass ratio of 41.4 g/kg, pH value of 6.40, and total nitrogen mass ratio of 15.06 g/kg, total phosphorus mass ratio of 15.23 g/kg, total potassium mass ratio of 20.11 g/kg, alkali nitrogen mass ratio of 154.36 mg/kg, the effective phosphorus mass ratio of 25.33 mg/kg and the available potassium mass ratio of 157.25 mg/kg.

**Test design:** The experiment used saturated D311 optimal

design (Xu 1997) to study the effects of irrigation, nitrogen, and biochar on the  $CH_4$  emission during the growing season. The water and fertilizer were compared with the local farmers' application standards, specifically with the irrigation amount of 5000~10000 kg/hm<sup>2</sup>, nitrogen fertilizer (pure nitrogen) of 50~150 kg/hm<sup>2</sup>, and biochar of 0~40 t/hm<sup>2</sup>. The specific design scheme is given in Table 1 and Table 2.

The experiment consisted of 11 treatments, 3 repetitions, and random blocks. The area of each plot was 10 m × 10 m = 100 m<sup>2</sup>. The rice was also planted around the plot to add protection. The technical measures such as rice breeding, transplanting, plant protection and pesticide use, and the same field management conditions were maintained in order to reduce the impact of lateral infiltration on the test. The cell and the community were treated with an isolation treatment, that is, a plastic plate and cement concrete were used to check seepage in the surrounding areas. The material was buried 40 cm deep below the surface of the field. The irrigation method adopts pipeline water supply, and each pipeline was equipped with a water meter to control the irrigation amount. The nitrogen fertilizer was applied according to the ratio of base fertilizer, manure fertilizer and panicle fertilizer to 5:3:2, and P fertilizer was applied as base fertilizer one, and the application amount was 45 kg/hm<sup>2</sup>. K base fertilizer and 8.5 leaf age (spotted differentiation period) were applied twice, the ratio was 1:1, the application amount was 80 kg/hm<sup>2</sup>; biochar was applied to the soil surface, and the charcoal was ploughed with a rotary tiller. The layers of soil were evenly mixed. The tested fertilizers were urea (including N 46%), diammonium phosphate (including N 18%, containing  $P_2O_5$  46%), potassium fertilizer ( $K_2O$  content 40%), and the tested biochar was straw biochar products of Liaoning Jinhufu Agricultural Development Co., Ltd.

The tested rice variety was the local main plant variety Longqingdao No.3, the planting density was 4 per hole, the base fertilizer was applied on May 6, the transplanting was carried out on May 17, the manure was applied on May 31, the application of spike fertilizer was carried out on July 19, and it was harvested on September 20. The growth period of rice is 127 days, which is divided into the regreening period (May 17th to May 30th), the tillering period (May 31st to July 7th), and the jointing and booting stage (July 8th to July 25th), heading flowering period (July 26 to August 4), milk ripening period (August 5 to August 24), and yellow ripening period (August 25 to September 20).

**Gas collection and determination:** Gas sampling was chosen on a sunny day using static dark box-gas chromatography. The box body was a rectangular parallel piped with a length of 18 cm on the side of the cross section. It is made of plexiglass, and the outer surface of the box is covered with

Table 1: Factor level coding table.

Coding value			Real value		
X <sub>1</sub>	X <sub>2</sub>	X <sub>3</sub>	W(m <sup>3</sup> /hm <sup>2</sup> )	N(kg/hm <sup>2</sup> )	BC(t/hm <sup>2</sup> )
2	2	2	7500	150	40
1.414	1.414	1	6800	135	30
0	0	0	5000	100	20
-1.414	-1.414	-1	3200	65	10
-2	-2	-2	2500	50	0

Table 2: Saturated D-311 optimal design processing table.

No.	Coding value			Real value			N <sub>2</sub> O Emission (kg/hm <sup>2</sup> )
	X <sub>1</sub>	X <sub>2</sub>	X <sub>3</sub>	W(m <sup>3</sup> /hm <sup>2</sup> )	N(kg/hm <sup>2</sup> )	BC(t/hm <sup>2</sup> )	
1	0	0	2	5000	100	40	0.158
2	0	0	-2	5000	100	0	0.199
3	-1.414	-1.414	1	3200	65	30	0.289
4	1.414	-1.414	1	6800	65	30	0.177
5	-1.414	1.414	1	3200	135	30	0.511
6	1.414	1.414	1	6800	135	30	0.178
7	2	0	-1	7500	100	10	0.015
8	-2	0	-1	2500	100	10	0.361
9	0	2	-1	5000	150	10	0.338
10	0	-2	-1	5000	50	10	0.170
11	0	0	0	5000	100	20	0.168

a heat insulating material (sponge and aluminium foil) to reduce the temperature change of the gas in the tank due to solar radiation during sampling. The box height was 90 cm in the early stage of rice growth, and the box height increased to 130 cm after the heading period. A three-way valve air hole was provided at a side of the box 30 cm from the top for connecting the three-way valve for collecting gas. There was a built-in fan at the top of the sampling box, which was used to mix the gas in the tank during sampling. Before the transplanting, the wooden base was placed in the sampling basin, and the base is flush with the mud surface. When sampling, the sampling box was lightly placed on the base of the return frame, and the water in the base water tank ensures the gas isolation inside and outside the box during sampling. The rice was transplanted for 1 week and the detection time was from 10:00 to 12:00 (Li et al. 1998, Epstein & Burke 1998). Each treatment was repeated three times in parallel, once a week, and ended one week before harvest. At the time of sampling, approximately 100 mL of gas in the tank was extracted with a syringe, samples were collected at 0, 5, 10 and 15 min, and then the gas in the syringe was immediately transferred to an aluminium foil sampling bag, and the sampling bag was brought back to the laboratory for measurement.

The concentration of the gas CH<sub>4</sub> was detected by

Shimadzu GC-14B gas chromatograph. The detectors were the flame ion detector of hydrogen FID and thermal conductivity detector TCD. The temperature was 200°C and 100°C. The separation materials were GDX-502 and Porapak Q respectively. The column temperatures were 100°C and 55°C, respectively, and the standard gas was supplied by the National Standards Center.

**Calculation methods and data analysis:** Calculation formula for the emission flux of rice field N<sub>2</sub>O (Zheng et al. 1998):

$$F = \rho \cdot h \cdot dc/dt \cdot 273 / (273 + T) \quad \dots(1)$$

Where, F is the gas discharge flux (mg.m<sup>-2</sup>.h<sup>-1</sup>), ρ is the gas density under standard conditions (kg.m<sup>-3</sup>), h is the box height (m), and dc/dt is within the sampling box. The gas concentration change rate (mL.m<sup>-3</sup>.h<sup>-1</sup>), 273 is the gas equation constant, and T is the average temperature (°C) in the sampling tank during the sampling process. The gas emission flux was calculated according to the curve of the concentration of the gas sample and the time. The growth season was the product of the average flux value of each growth period and the total length of the growth period and then accumulated and obtained (Zhang et al. 2011).

The test data were statistically analysed using Excel 2003, SPSS 17.0 and MATLAB 7.0.

**RESULTS AND ANALYSIS**

**N<sub>2</sub>O growth season emission effect function:** The X1(W), X2(N), and X3(C) code values in Table 1 are independent variables. The average value of N<sub>2</sub>O growth season emissions in Table 2 is the quadratic polynomial regression analysis of the dependent variables. The regression equation between N<sub>2</sub>O emissions and irrigation amount, nitrogen fertilizer and biochar was obtained as below.

$$Y = 0.1677 - 0.0114 X_1 + 0.072 X_2 - 0.0103 X_3 + 0.0166 X_1 X_2 - 0.0273 X_1 X_3 + 0.0299 X_2 X_3 + 0.0018 X_1^2 + 0.0183 X_2^2 + 0.0027 X_3^2$$

The F test was performed on the regression equation:  $F = 4.75 > (F_{0.01}(10, 20)) = 3.37$ , and the regression equation is extremely significant, that is, the equation can reflect the relationship of N<sub>2</sub>O growth season emissions and irrigation amount, nitrogen fertilizer and biochar. The absolute value of the primary coefficient of the regression equation is the basis for judging the influence of various factors on N<sub>2</sub>O emissions. Therefore, from the equation it can be seen that the degree of influence on N<sub>2</sub>O emissions is: nitrogen fertilizer > water > biochar.

**Single factor effect analysis:** The above-mentioned main effect model adopts the “dimension reduction method”, and any two factors are set at zero code value, and the effect of single factor on the growth of N<sub>2</sub>O growth season is obtained. The single factor effect equation was obtained and the single factor effect curve was drawn in Fig. 1.

$$Y_1 = 0.1677 - 0.0114X_1 + 0.0018X_1^2$$

$$Y_2 = 0.1677 + 0.072X_2 + 0.0183X_2^2$$

$$Y_3 = 0.1677 - 0.0103X_3 + 0.0027X_3^2$$

It can be seen from Fig. 1 that within the range of coded values, the effect of irrigation amount and biochar on N<sub>2</sub>O

emissions has an inhibitory effect, and the increase of nitrogen fertilizer can significantly promote N<sub>2</sub>O emissions.

**Factor interaction effect analysis:** Set any one factor to zero code value to get the interaction effect equation of the other two factors. The equation is as follows:

$$Y_{12} = 0.1677 - 0.0114X_1 + 0.072X_2 + 0.0166X_1X_2 + 0.0018X_1^2 + 0.0183X_2^2$$

$$Y_{13} = 0.1677 - 0.0114X_1 - 0.0103X_3 - 0.0273X_1X_3 + 0.0018X_1^2 + 0.0027X_3^2$$

$$Y_{23} = 0.1677 + 0.072X_2 - 0.0103X_3 - 0.0299X_2X_3 + 0.0183X_2^2 + 0.0027X_3^2$$

This two-factor interaction effect equation is plotted in Fig. 2. It can be seen from Fig. 2 that the interaction between water and nitrogen fertilizer can promote the emission of N<sub>2</sub>O. The interaction between water and biochar can inhibit the emission of N<sub>2</sub>O. Nitrogen fertilizer and biochar can promote the emission of N<sub>2</sub>O. When the irrigation amount and biochar were fixed at a certain level, the increase of nitrogen fertilizer application had a significant effect on the promotion of N<sub>2</sub>O emission.

**Analysis of water/fertilizer and biochar management optimization:**

The frequency effect analysis method was used to optimize the main effect model, and the coded values are divided into five levels (-2, -1.414, 0, 1.414, 2) within the experimental design range, which constitute  $T = 53 = 125$  processing combinations, the combined output increased the growth rate of N<sub>2</sub>O growth season in paddy fields to 10%. Because the factors of treatment 11 in this experiment are all at zero level, it is considered normal treatment, that is, the normal emission of N<sub>2</sub>O growth season is selected 100%~110% (0.157~0.174 kg/hm<sup>2</sup>) for frequency analysis, and 5 N<sub>2</sub>O growth season water and fertilizer and biochar management simulation equations were obtained.

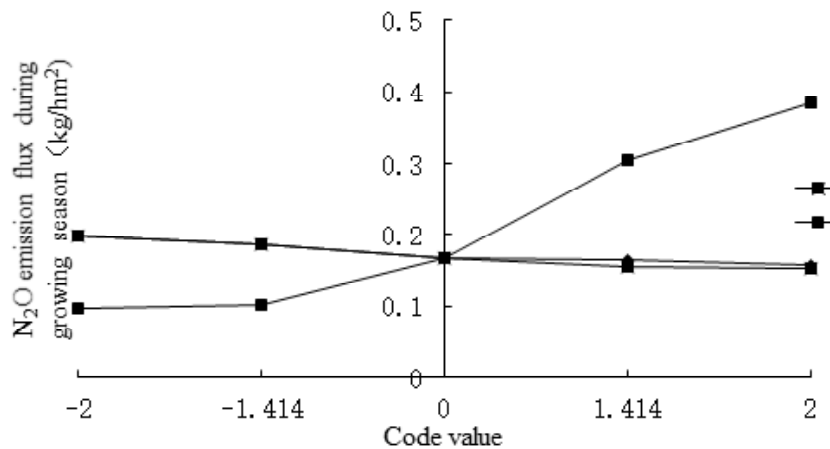
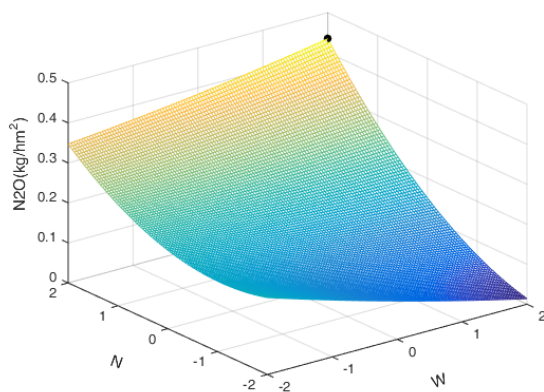
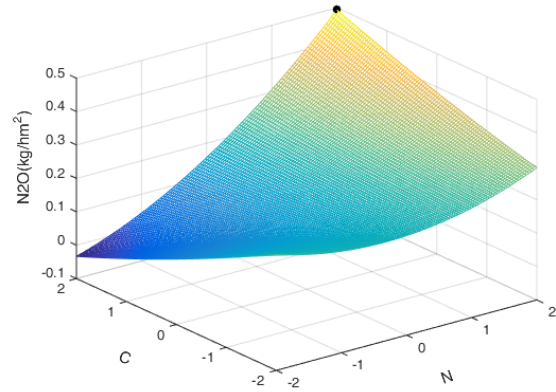


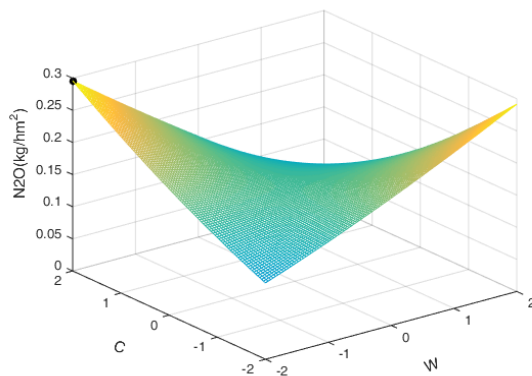
Fig. 1: Single factor effect curve.



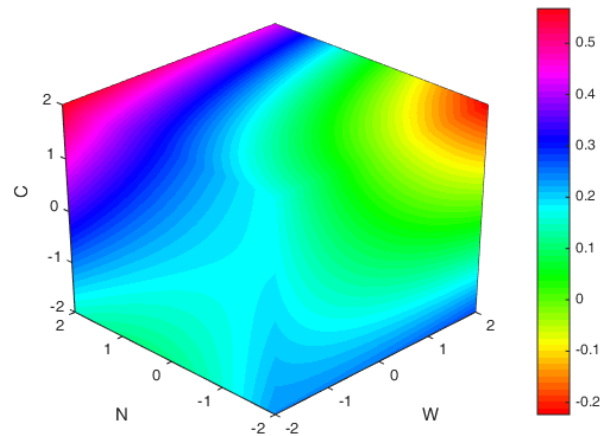
(a) Surface diagram of irrigation amount and nitrogen fertilizer interaction effect.



(b) Surface diagram of irrigation amount and biochar interaction effect.



(c) Surface diagram of nitrogen and biochar interactions.



(d) Four-dimensional map of irrigation, nitrogen and biochar interactions.

Fig. 2: Analysis of two factors interaction effects of methane growth season emissions.

The frequency analysis of gas emission flux is given in Table 3.

## DISCUSSION

The amount of irrigation has an important impact on the N<sub>2</sub>O emission in paddy fields. Studies have shown that as the amount of irrigation increases, not only the diffusion of O<sub>2</sub> into the soil receives restrictions, but also the movement, distribution and release of denitrifying gases in the soil, along with N<sub>2</sub>O. The prolongation of the residence time in the soil has further increased by the possibility of further reduction to N<sub>2</sub>, which resulted in a decrease in N<sub>2</sub>O emissions (Zhang et al. 2011), which is in agreement with the results of this test. The experiment also showed that the application of nitrogen fertilizer application from the low level to the high level has a significant effect on the growth

of N<sub>2</sub>O growth season in paddy fields, and the promotion of high nitrogen level is more significant. This is consistent with the results of the current literature review. Cai et al. (2008) studied the effects of nitrogen fertilizer application on N<sub>2</sub>O emissions in the black soil test base of Gongzhuling City, Jilin Province through culture experiments. The results showed that nitrogen fertilizer had the most obvious impact on N<sub>2</sub>O emissions. Jiao et al. (2008) studied the effects of nitrogen fertilizer levels on N<sub>2</sub>O emissions from different soils through pot experiment. The results showed that the increase of nitrogen fertilizer application promoted N<sub>2</sub>O emissions in the rice-growing season significantly. The reason may be that the application of nitrogen fertilizer can provide sufficient nitrogen source for the soil, and the nitrification and denitrification in the soil have enhanced, which is resulting in a large amount of N<sub>2</sub>O emissions.

Table 3: Water, fertilizer and biochar application schemes for N<sub>2</sub>O growth season emissions of 0.157~0.174 kg/hm<sup>2</sup>.

Coding value	Irrigation amount		Nitrogen fertilizer		Biochar	
	No. of times	Frequency, %	No. of times	Frequency, %	No. of times	Frequency, %
-2	1	20	1	20	1	20
-1.414	2	40	1	20	1	20
0	1	20	2	40	1	20
1.414	1	20	1	20	1	20
2	0	0	0	0	1	20
Average value	-0.039		0.408		0.003	
Standard error	0.218		0.142		0.228	
Confidence interval (95%)	-0.598~0.425		0.132~0.694		-0.487~0.442	
Optimization plan (kg/hm <sup>2</sup> )	4252~5531		103.30~117.35		15.12~24.42	

The formation of soil N<sub>2</sub>O is mainly produced by nitrification and denitrification with the participation of soil microorganisms. Li et al. (2012) and Zhang et al. (2012) pointed out that with the increase of biochar application, the effect of biochar on soil N<sub>2</sub>O emission reduction has gradually enhanced, which is consistent with the results of this study. The reason for this phenomenon may be as follows: After the biochar is applied to the soil, the soil bulk density is reduced, the soil aeration is improved, and the higher C/N value of the biochar itself inhibits the transformation and denitrification of the nitrogen microorganisms (Lehmann et al. 2006). Biochar increases the cation exchange capacity of the soil, and the large specific surface area of the biochar itself can adsorb more NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup> and phosphate, which are likely to cause N<sub>2</sub>O increase (Mizuta et al. 2004, Hua et al. 2013). Some components contained in biochar inhibit the activity of NO<sub>3</sub>-N to N<sub>2</sub>O conversion key enzymes, or promote the activity of N<sub>2</sub>O to N<sub>2</sub> conversion reductase (Rondon et al. 2006, Yanai et al. 2007), and ultimately reduce soil N<sub>2</sub>O emissions.

In recent years, blindly applying nitrogen fertilizer in pursuit of rice yield and neglecting the impact on the environment, this study attempts to add biochar to the soil, which also co-couples with water and fertilizer to establish the N<sub>2</sub>O growth season emissions of paddy fields in the north-east cold region. The mathematical model of nitrogen fertilizer and biochar can reflect the relationship between N<sub>2</sub>O emission in paddy field and water and fertilizer and biochar through the significance test, which makes the quantitative study of water and fertilizer and biochar more convenient and has a good application prospect. However, the effects of water-fertilizer and biochar coupling effects on the seasonal emissions of N<sub>2</sub>O in paddy fields have been only discussed. No qualitative research is carried out. In future in-depth research, data from years and different growth stages should be accumulated to make the model perfect. Therefore, it has a practical guiding significance.

## CONCLUSION

1. Water, nitrogen, and biochar have different effects on the N<sub>2</sub>O growth season in paddy fields. The analysis results show that the effects of three factors on N<sub>2</sub>O emissions are as follows, nitrogen fertilizer>water>biochar. The increase of irrigation amount and biochar has an inhibitory effect on N<sub>2</sub>O emissions, and the increase of nitrogen fertilizer can significantly promote N<sub>2</sub>O emissions.
2. The analysis of the interaction of the two factors on the growth of N<sub>2</sub>O growth season shows that the interaction of water and nitrogen fertilizer can promote the emission of N<sub>2</sub>O. The interaction between water and biochar has an inhibitory effect on N<sub>2</sub>O emissions, and nitrogen and biochar contribute to N<sub>2</sub>O emissions. When the irrigation amount and biochar are fixed at a certain level, the increase of nitrogen fertilizer application has a significant effect on the promotion of N<sub>2</sub>O emission.
3. Combining the yield, when controlling the increase of the N<sub>2</sub>O growth season in the paddy field, the increase range was controlled within 10%, and the main effect model is optimized by the frequency analysis method. The optimized water and biochar application scheme is: Irrigation amount is 4252~ 5531kg/hm<sup>2</sup>, nitrogen application rate is 103.30~117.35kg/hm<sup>2</sup> and biochar input amount is 15.12~24.42t/hm<sup>2</sup>.

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