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Effect of the Slow-Release Nitrogen Fertilizer Oxamide on Ammonia Volatilization and Nitrogen Use Efficiency in Paddy Soil

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Received: 16 March 2018; Accepted: 16 April 2018; Published: 18 April 2018

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Abstract: The effects of a single basal fertilization with oxamide compared with those of a split application of urea on ammonia volatilization, rice yield, nitrogen (N) accumulation, and N use efficiency were investigated in a field experiment over 2 years. The study consisted of two N fertilizers (oxamide and urea) applied at 157.5 and 225 kg N ha^{-1} and a no-N Control. Compared with urea, the single application of oxamide produced similar rice yields and reduced approximately 38.3% to 62.7% of the N lost through ammonia volatilization in 2013 and 2014. Oxamide applied at a rate of 225 kg N ha^{-1} resulted in greater aboveground accumulation of N by rice than the other treatments in both years, and oxamide fertilization resulted in the accumulation of an additional 15.2 kg N ha^{-1} and 15.3 kg N ha^{-1} compared to the amounts accumulated under the urea treatments at the same N application rates. N use efficiency was higher under oxamide than under urea treatment. In conclusion, the use of oxamide as a fertilizer can reduce N loss via ammonia volatilization, increase N use efficiency, and maintain a steady rice grain yield.

Keywords: oxamide; yield; ammonia volatilization; N use efficiency; rice

1. Introduction

Nitrogen (N) management involves selecting a proper application rate, source, timing, and placement, and it plays an important role in increasing rice yield. Increasing N fertilizer application has been a major approach that has significantly contributed to the improvement of rice yield [1]. However, excessive chemical N inputs and improper methods of fertilization have led to low N use efficiency and have resulted in a series of environmental problems due to leaching, runoff, and the emission of ammonia and greenhouse gases [2–8]. The traditional fertilization method is labor intensive because of the split application of N fertilizer (at least half of the total amount of N is applied as a basal dressing and the rest of the fertilizer are later applied as top dressings). However, the lack of fertilizer application machines and the shortage of agricultural workers in China make it difficult [9]. Hence, more effective N management strategies with an emphasis on being environmentally friendly, convenient application, and high N use efficiency are urgently needed.

The application of a slow- or controlled-release fertilizer is an effective approach to increasing N use efficiency, because these fertilizers supply N on a time schedule that aims to be better synchronized with crop demand, thereby decreasing environmental losses of N [10–13]. Oxamide, which is a diamide of oxalic acid that contains 31.8% N, is slightly water soluble, and is chemically and physiologically neutral, is suggested to be an effective type of slow-release fertilizer [14–16].

Because of sparing solubility and slowly hydrolysis [14], oxamide releases N slowly and constantly. These properties suggest that oxamide might be a useful alternative to soluble N fertilizers. However, during the last few decades, there have only been a few studies concerning on the use of oxamide as a slow-release fertilizer because at that time it was too expensive for commercial usage [17]. Furthermore, most of the experiments in those studies were conducted indoors or under pot culture conditions, and very little effort was made to investigate the behavior of oxamide in field experiments [18]. Progress has been made in the oxamide manufacturing process that renders the agricultural application of oxamide feasible; therefore, it is very important to determine the effects of oxamide as a slow-release fertilizer for rice in natural field conditions.

Therefore, in this experiment, a 2-year field study was conducted to determine the effects of two N application levels (157.5 and 225 kg N ha^{-1}) of oxamide applied as a single basal fertilization and urea applied as a split fertilization on rice yield, N use efficiency and NH_3 volatilization loss under field conditions. The primary objective of this study was to test the hypothesis that oxamide decreases the ammonia volatilization and increases the N use efficiency of rice.

2. Results and Discussion

2.1. Ammonia Volatilization

The main component of total reactive N in paddy soil is ammonia [19], and the emission of ammonia is the largest global contributor to N gases in the atmosphere [20]. The largest contribution to ammonia emissions comes from various agricultural practices, such as chemical N fertilizer application [21]. However, emissions vary from fertilizer to fertilizer [20]. In this experiment, the patterns of the daily ammonia volatilization rates due to oxamide applications were quite different from those due to urea applications. In the urea treatments, the ammonia volatilization rate reached a maximum 1 or 2 days after the urea was applied to the field and then decreased sharply after approximately 5–12 days, returning to a level similar to that of the control treatment. The peak ammonia volatilization rates in Ur-225 and Ur-157.5 were 12.4kg N ha^{-1} day^{-1}, 7.8 kg N ha^{-1} day^{-1} in 2013 and 3.7kg N ha^{-1} day^{-1}, 2.3kg N ha^{-1} day^{-1} in 2014, respectively (Figures 1 and 2). This result was consistent with the results of previously published studies [22]. In contrast, the ammonia volatilization rates in the oxamide treatments rose slowly during the first 8 days after the basal fertilization in 2013 and the first 10 days in 2014, which were significantly lower than urea; the ammonia volatilization rates reached their peak values on the 14th (2013) and 15th (2014) day and then maintained relatively steady levels until the 29th day in 2013 and the 33rd day in 2014 (Figures 1 and 2). The peak ammonia volatilization rates in Oa-225 and Oa-157.5 were 5.4 kg N ha^{-1} day^{-1}, 3.1 kg N ha^{-1} day^{-1} in 2013 and 1.6 kg N ha^{-1} day^{-1}, 0.9kg N ha^{-1} day^{-1} in 2014, respectively. This finding indicated that oxamide releases ammonium slower than urea when applied to a paddy field. Furthermore, regardless of the existing N resources, the ammonia volatilization rate increased with increasing N application rates (Figures 1 and 2), which was consistent with the results of Banerjee et al. [23] and Hayashi et al. [24]. Similar results were also observed by Chen et al. [25], who reported that NH_3 losses from volatilization increased linearly with increasing amounts of applied urea in paddy fields in the Erhai Lake Watershed, China.

Urea is the most widely used N source for rice in China, and the main N losses from urea applied to rice crops occur via ammonia volatilization. Han et al. [26] suggested that chemical N fertilizers, especially urea, contribute between 32% (1970) and 47% (2005) of the total global ammonia emissions because the rapid hydrolysis of urea leads to a high NH_4^+ concentration and, consequently, a high pH in floodwater [27]. In contrast, oxamide is only slightly soluble in water and believed to be mineralized and limited by microbial activity. When oxamide was applied to the rice field, there was no competition for N between the rice seedlings and the microorganisms for the first few days, and thus, a very limited amount of the oxamide fertilizer was mineralized, leading to a lower ammonia volatilization rate in the oxamide treatment than in the urea treatment. Then, as the rice plants started to grow vigorously, competition for N between the plants and the microbes prompted the microorganisms to mineralize oxamide-N to its mineral form, generating the increasing ammonia volatilization rate observed in the oxamide treatment.

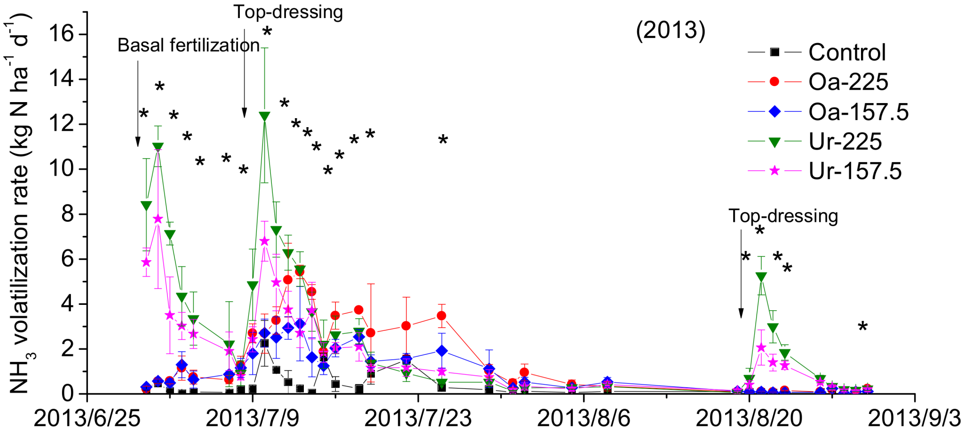

Figure 1. Changes in ammonia volatilization rates (kg N ha^{-1} day^{-1}) after N fertilization in 2013. Asterisks indicate significant differences (*p* < 0.05) among fertilization treatments.

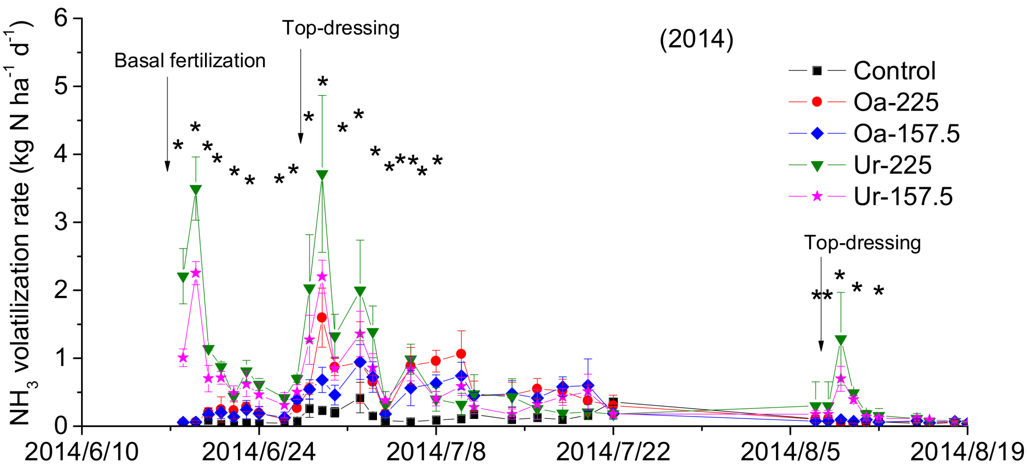

Figure 2. Changes in ammonia volatilization rates (kg N ha^{-1} day^{-1}) after N fertilization in 2014. Asterisks indicate significant differences (*p* < 0.05) among fertilization treatments.

Meteorological conditions, especially temperature and rainfall, strongly influence fluctuations in ammonia volatilization [28,29]. An increase in air temperature and a lack of rainfall may increase the ammonium-N concentration in floodwater and accelerate the movement of ammonia from the water surface [30], which triggers the ammonia volatilization process [31]. The results of this study show that the ammonia volatilization loss was higher in 2013 than in 2014 (Table 1), possibly because of the high temperature and low amount of precipitation in 2013 (Figure 3). In addition, a greater number of sunlight hours in 2013 (831 h) than in 2014 (423 h) may have promoted algal growth, causing a rise in floodwater pH and, consequently, an increase in ammonia volatilization [32,33] (Figure 3).

In both 2013 and 2014, the cumulative ammonia volatilization losses from the N fertilizer treatments were as follows: Ur-225 > Ur-157.5 > Oa-225 ≥ Oa-157.5 (Table 1). Consequently, the percentage of N lost was significantly higher in the urea treatment than in the oxamide treatment at the same N application rate. The application of oxamide reduced N lost to the environment by 38.3% to 62.7% through ammonia volatilization (Table 1). The major reason was that ammonia volatilization inhibited by slower hydrolysis of oxamide due to its slight water solubility. In addition, when urea was top dressed, it was broadcast on the soil surface, which encouraged N loss via ammonia volatilization. The hydrolysis of urea results in a rapid increasing of pH in surface water, which encourages NH_4^+ loss via ammonia volatilization.

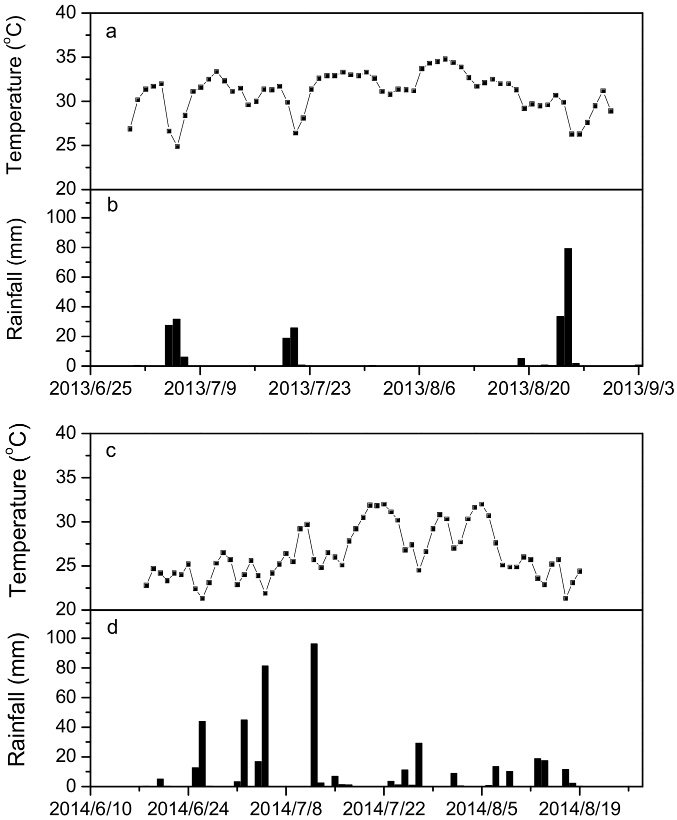

Figure 3. (**a**) Daily mean air temperature (symbols and lines) and (**b**) daily rainfall (columns) during the experimental period in 2013; (**c**) Daily mean air temperature (symbols and lines) and (**d**) daily rainfall (columns) during the experimental period in 2014. The meteorological data during the NH_3 volatilization measurement period were obtained from the Meteorological Station of Danyang City.

Table 1. Cumulative ammonia volatilization from N fertilization and the percentage of N lost relative to the total N applied in the 2013 and 2014 rice growing seasons.

Treatment	2013		2014	
	N Lost via NH_3 Volatilization	N Lost Out of the Total N Applied	N Lost via NH_3 Volatilization	N Lost Out of the Total N Applied
	kg N ha^{-1}	%	kg N ha^{-1}	%
Oa-225	59.5 bc	26.4 b	9.22 c	4.10 b
Oa-157.5	38.0 c	24.1 b	7.28 c	4.62 b
Ur-225	96.4 a	42.8 a	24.7 a	11.0 a
Ur-157.5	66.4 b	42.2 a	17.2 b	10.9 a

Different letters within a column refer to significant differences ($p < 0.05$) among treatments.

2.2. Rice Yield, N Accumulation, and N Use Efficiency

N fertilization significantly affected the grain yields. In both years, the addition of N fertilizer resulted in greater rice production than in the control treatment; however, there were no statistically significant differences in rice production according to different N sources at equivalent N rates or according to different N rates with the same N sources (Table 2). The rice yield for one application of oxamide was similar to that with urea applied in three split applications. Reduction in the number of fertilization events saves labor and hence provides economic benefits.

The rice yield levels differed between 2013 and 2014. During the rice growth period, particularly during the flowering and filling stages, climatic factors such as a suitable temperature and sufficient sunlight play important roles in achieving high yields. The climatic conditions in 2013 were favorable for the growth of rice.

Table 2. Yields of rice under different fertilization treatments in 2013 and 2014.

Treatment	Grain Yield (t ha^{-1})		
	2013	**2014**	**Average**
Control	6.47 c	4.71 c	5.59 c
Oa-225	8.57 a	7.65 a	8.11 a
Oa-157.5	8.17 ab	7.41 ab	7.79 ab
Ur-225	8.30 ab	7.37 ab	7.84 ab
Ur-157.5	8.06 b	7.09 b	7.57 b

Different letters within a column refer to significant differences (p < 0.05) among treatments.

The amount of N accumulated in the aboveground biomass (straw and grain) in both 2013 and 2014 could be ranked as follows: Oa-225 > Ur-225 $\geq$ Oa-157.5 > Ur-157.5 > Control (Table 3). According to the statistical analysis, in 2013, N accumulation in both grain and straw was significantly higher under oxamide fertilization than under urea fertilization for the same N application rate, which was compatible with the result of the study by Li et al. [33]. However, that trend was not observed at the 225 kg N ha^{-1} application rate in 2014. Because the rice yields were higher in 2013 than in 2014, the N requirements were also much greater in 2013 than in 2014. The advantages of oxamide on crop N accumulation, as a slow-release N fertilizer, were particularly apparent at the high application rate. However, the relatively low rice yield in 2014 combined with less N lost through NH_3 volatilization, reduced the N requirement, and therefore, the urea treatment at the high application rate could provide sufficient N for the rice growth. Thus, in 2014, there was no significant difference in N accumulation under oxamide and urea fertilization at the 225 kg N ha^{-1} rate. The N use efficiency was improved by reducing the N application rate (Table 4). Similar results were also observed by Zhang et al. [34], who reported that the N use efficiencies at low N rates were higher than those at high N rates. In this study in 2013, the N use efficiencies were 40.25%, 46.54%, 33.50%, and 38.67% with the application of oxamide and urea at different rates, respectively (Table 4). The application of oxamide significantly increased the N use efficiency in 2013. However, in 2014, the N use efficiency was not significantly different between oxamide and urea treatments (Table 4).

Table 3. Total N accumulated by rice aboveground biomass under different fertilization treatments in the 2013 and 2014 rice seasons.

Treatment	N Accumulation in 2013 (kg N ha^{-1})			N Accumulation in 2014 (kg N ha^{-1})		
	Grain	**Straw**	**Total**	**Grain**	**Straw**	**Total**
Control	82.35 c	32.86 d	115.2 d	55.00 c	25.53 c	80.53 d
Oa-225	128.4 a	77.36 a	205.8 a	114.7 a	72.52 a	187.3 a
Oa-157.5	122.5 b	65.97 b	188.5 b	96.51 b	64.96 ab	161.5 b
Ur-225	120.9 b	69.64 b	190.6 b	102.2 ab	69.83 a	172.0 ab
Ur-157.5	118.3 b	57.82 c	176.1 c	91.07 b	51.41 b	142.5 c

Different letters within a column refer to significant differences (p < 0.05) among treatments.

Table 4. The N use efficiency of rice under different fertilization treatments in the 2013 and 2014 rice seasons.

Treatment	N Use Efficiency (%)	
	2013	2014
Oa-225	40.25 b	47.44 a
Oa-157.5	46.54 a	50.48 a
Ur-225	33.50 c	40.64 a
Ur-157.5	38.67 b	42.86 a

Different letters within a column refer to significant differences ($p < 0.05$) among treatments.

3. Materials and Methods

3.1. Soil Properties and Site Description

The experiment was located in Danyang (31°59′37.8′′ N, 119°30′14.1′′ E), Jiangsu Province, China, in the lower reaches of the Yangtze River. A portion of a paddy field that is surrounded by large paddy fields cultivated by other local farmers was selected for this experiment. The soil (0–20 cm depth) at the site was classified as a hydromorphic paddy soil with pH (soil/water, 1:2.5) of 6.62, organic matter content of 22.79 g kg^{-1}, total N of 1.41 g kg^{-1}, alkali-hydrolyzable N of 118.91 mg kg^{-1}, available phosphorus of 7.97 mg kg^{-1}, and available potassium of 83.23 mg kg^{-1}.

In this area, the following cultivation and field management practices are usually adopted in paddy fields with rice and wheat crop rotations. First, approximately 220–260 and 200–230 kg N ha^{-1} of N fertilizers are routinely applied to the soil to grow rice in the summer and wheat in the winter, respectively. In addition, 50% of the N is applied basally, 30% is top-dressed during the tillering stage, and the remaining 20% is top-dressed during the ear differentiation stage for each crop. Second, direct sowing and surface fertilizer application are employed due to their convenience and low cost. Third, flooded water is mostly maintained at a depth of 5 cm in the field during rice seasons except when it is drained before sowing, several times midseason for aeration and at the end of the season. Fourth, phosphate and potassium fertilizers are applied basally in the form of superphosphate at an average rate of 70 kg P_2O_5 ha^{-1} and in the form of potassium chloride at an average rate of 40 kg K_2O ha^{-1}.

This location has a subtropical monsoon climate and had an average temperature during rice growth of 31 °C and 26.3 °C in 2013 and 2014, respectively (Figure 3a,c). In addition, the daily average air temperature at the experimental site during the experimental period varied from 24.9 to 34.8 °C and from 21.3 to 32 °C in 2013 and 2014, respectively (Figure 3a,c). There were 32 more days during the experimental period with daily air temperatures ≥30 °C in 2013 than in 2014. The total rainfall from 30 June to 30 August 2013 was 229.9 mm, and from 18 June to 19 August 2014 it was 443.1; 14 and 30 rainfall events occurred during the experimental period in 2013 and 2014, respectively (Figure 3b,d). Both the amount and frequency of rainfall during the experiment period were higher in 2014 than in 2013.

3.2. Experimental Design

The experiment was a randomized complete block (plot size: 12.5 m × 4 m) design with three replicates and consisted of five treatments: (1) no N fertilizer Control; (2) urea (46% N) treatment at 225 kg N ha^{-1} (Ur-225) and (3) 157.5 kg N ha^{-1} (Ur-157.5); (4) oxamide (31.8% N, 2.00–3.36 mm diameter) treatment at 225 kg N ha^{-1} (Oa-225) and (5) 157.5 kg N ha^{-1} (Oa-157.5). Fifty percent of the total amount of urea was applied as a basal dressing 1 d before the rice was transplanted, while the rest of the urea was applied as two top dressings, once at the beginning of the tillering stage (30%) and once at the onset of the booting stage (20%). All oxamide treatments with 2.00–3.36 mm diameter granules were basally applied. Basal fertilizers, including all of oxamide and 50% of urea were broadcasted and well mixed with soil by plowing and levelling, and top-dressed urea was broadcasted on the field surface. The dates of basal dressing and top dressing were 30 June, 9 July, and 19 August in 2013 and 18 June, 29 June, and 8 August in 2014. All treatments also received 40 kg K_2O ha^{-1} and 70 kg P_2O_5 ha^{-1}.

3.3. Sampling and Measurements

3.3.1. Ammonia Volatilization

The ammonia volatilization rate was estimated by using the continuous air flow enclosure method [35]. The system consisted of a dynamic chamber, a chemical trap, and a vacuum pump (Figure 4). The dynamic chamber, with an inner diameter of 200 mm and a height of 150 mm, was cylindrical and made from plexiglass. When measuring NH_3 volatilization, the chamber was inserted into the surface water and soil to a depth of 12 cm. Then, the NH_3 was determined by drawing air through the vacuum system and passing the air through an acid trap containing 50 mL of 0.01 M H_2SO_4. The air exchange rate was set to approximately 15–20 times the chamber volume per minute. NH_3 volatilization was measured twice a day, once in the morning (9:00 to 11:00) and once in the afternoon (14:00–16:00). The ammonium N content of the traps was determined colorimetrically using the indophenol reaction method. The NH_3 volatilization was measured every day for the first week after the N fertilizer application (the measurement was cancelled if it rained heavily), every other day the next week, and then every 2–3 days until there were no significant differences among the treatments. The daily NH_3 volatilization flux was calculated as the average of the rates measured each day. Any NH_3 volatilization rates that were not measured were estimated by averaging the values around them. The total NH_3 volatilization loss was calculated as the sum of the daily volatilization losses measured and estimated over the measurement period.

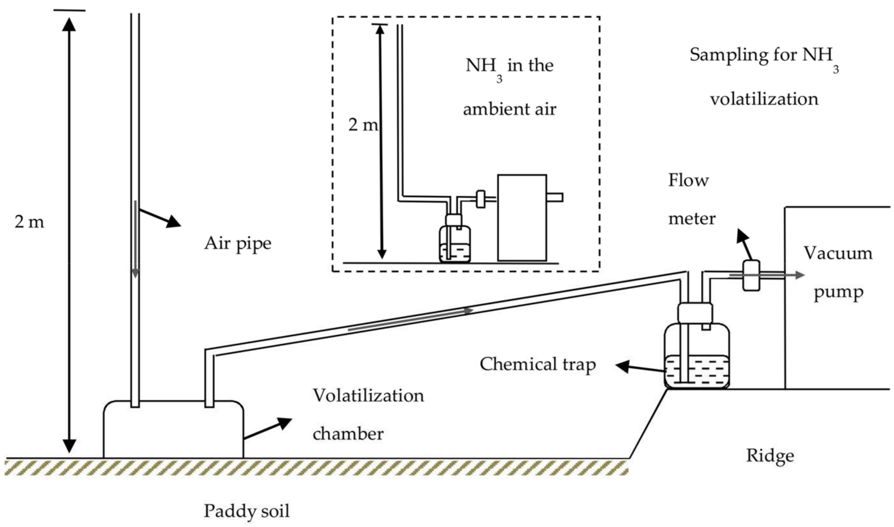

Figure 4. Schematic diagram of the continuous air flow enclosure method.

3.3.2. Grain Yield and N Accumulation

Rice plant samples were taken from a 1 m × 1 m area in the middle of each plot, divided into two parts (grain and straw), and dried to determine the dry weight and the ratio of straw to grain. Then, the crop was manually harvested from the entire area of each plot, cleaned, and dried in the sun to determine the rice grain yield. The plant samples were ground to pass through a 0.5 mm sieve and digested with H_2SO_4–H_2O_2. The total N concentration was measured by a continuous-flow injection analyzer (AA3, Bran and Luebbe, Norderstedt, Germany) [36]. The N accumulated by the plants was calculated by multiplying the dry matter by the total N concentration. The N use efficiency was calculated as the percentage of the applied N fertilizer recovered in the aboveground biomass of the plants that received the Ur-225, Ur-157.5, Oa-225, and Oa-157.5 treatments minus the N in the aboveground biomass of the plants that received the control treatment [37].

3.4. Statistical Analysis

Data were subjected to analysis of variance (one-way ANOVA), and significant differences in means among treatments were compared by Duncan's multiple comparisons test at a significance level of $p < 0.05$ with SPSS 16.0 software (IBM SPSS Statistics, Armonk, NY, USA).

4. Conclusions

Our results indicated that singly-applied oxamide does not result in a decrease in rice yield, compared with split applied urea at the same rate. Oxamide application is effective at improving N use efficiency, decreasing N losses through ammonia volatilization. But, benefits may vary from year to year and will be reduced or absent in years where yield potential is lower and there is sufficient N as it is. The use of oxamide could also save labor by reducing the number of top-dressing events. Thus, the use of oxamide has better economic and environmental effects than the use of urea.

Acknowledgments: This research was supported by the National Key Research and Development Program of China (No. 2017 YFD0800103), Science and Technology Service Network Program of Chinese Academy of Sciences (KFJ-SW-STS-142) and the Science and Technology Support Program of Jiangsu Province, China (BE 2012407). The authors thank the Jiangsu Danhua Group Co., Ltd. (Danyang, China) for providing the oxamide fertilizer.

Author Contributions: Contributions: Y.T. and Z.D. conceived and designed the study; data collection was performed by Y.T. in close collaboration with X.L. and W.S.; all authors participated in the analysis of the data; Y.T. wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest.

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