INTRODUCTION

Rice (Oryza sativa L.) is one of the major staple food crops in China. However, rice culture has been traditionally carried out to obtain either maximum yield or high quality rice, or both. These goals have been achieved by applying fertilizers well in excess of paddy nutrient requirements (Maruyama et al., 2008). Its total fertilizer consumption reached 46.3 billion kg in 2004 in China, over one-third of the world’s consumption (Zhu et al., 2006). Its partial factor productivity from applied Nitrogen (N) decreased from 55.0 to 20.0 kg/ha from 1977 to 2005 (Ju et al., 2009). Consequently, the excessive use of fertilizers with decreasing fertilizer use efficiencies in agriculture has resulted in large amounts of nutrient entering ambient water bodies and the atmosphere through various means (Wortmann and Walters, 2006; Yoshinaga et al., 2007; Ni et al., 2007; Chirinda et al., 2010; Li et al., 2008). A recent investigation of 67 main lakes around China revealed that 80% of these had been polluted to a level of grade IV (unhealthy for human contact) or lower. Only about 20% of the lakes had relatively good qualities, ranging from the grade II-III (Li et al., 2006). N and P losses from agricultural fields are the main causes of the eutrophication of these lakes. Previous study showed that losses from N fertilizers are dependent on its form and other management factors (Mengel, 1992). So, it is an urgent problem that how to release nitrogen input and losses under not reducing crops production.

During the last three decades, many coated fertilizers have been developed for agricultural and...
horticultural crops. These products are generally referred to as Controlled-Release Fertilizers (CRF) or Slow-Released Fertilizers (SRF) due to their unique characteristics of nutrient release over an extended period. The slow-released fertilizer and controlled-release fertilizers are made to release their nutrient contents gradually and to coincide with the nutrient requirement of a plant. These fertilizers can be physically prepared by coating granules of conventional fertilizers with various materials that reduce their dissolution rate (Ge et al., 2002; Shavit et al., 2002). So, nutrient uptake efficiency is greater and leaching losses are lower for CRF products as compared to readily available forms of fertilizers (Dou and Alva, 1998). The release and dissolution rates of water-soluble fertilizers depend on the coating materials. This brings about the idea of developing the entrapped within period. The slowNreleased fertilizer and controlled N better survival in inoculated soils, allowing for their readily available forms of fertilizers (Dou and Alva, 1998). The release and dissolution rates of water-soluble fertilizers depend on the coating materials. This brings out the idea of developing the entrapped within nano-materials (Teodorescu et al., 2009). Consequently, the fertilizers are protected by the nano-materials for better survival in inoculated soils, allowing for their controlled release into the soil (Saigusa, 2000).

Materials with a particle size less than 100 nm in at least one dimension are generally classified as nano-materials. The development of nanotechnology in conjunction with biotechnology has significantly expanded the application domain of nano-materials in various fields. A variety of carbon-based, metal and metal oxide-based dendrimers (nano-sized polymers) and bio-composites nano-materials (Byrappa et al., 2008; Qureshi et al. 2009) are being developed. Types include single-walled and multi-walled carbon nanotubes, magnetized iron (Fe) nano-particles, Aluminum (Al), Copper (Cu), gold (Au), silver (Ag), Silica (Si), Zinc (Zn) nano-particles and Zinc Oxide (ZnO), Titanium dioxide (TiO$_2$) and Cerium Oxide (Ce$_2$O$_3$), etc. General applications of these materials are found in water purification, wastewater treatment, environmental remediation, food processing and packaging, industrial and household purposes, medicine and in smart sensor development (Byrappa et al., 2008; Qureshi et al., 2009; Shan et al., 2009; Lee et al., 2010; Bradley et al., 2011; Zambrano-Zaragoza et al., 2011). However, in the field of agriculture, the use of nano-materials is relatively new and needs further exploration. Due to its high surface energy and chemical activity, the combination of slow-released fertilizers and nano-materials may improve the nutrition of plants and mitigate the environmental impact from water-soluble fertilizers.

On the basis of the above background, we incorporated in this study nano-carbon was into slow-released fertilizer and the influence on rice yield, nitrogen use efficiency and nitrogen loss in surface water of paddy soil was conducted by field experiment. The aim of the present study is to reveal whether nano-carbon is used as coating material for slow-released fertilizer and benefit for the environment.

### MATERIALS AND METHODS

The experiment was conducted at the base of school of agriculture, Yangtze University, in 2010, which is located at 111°150′ E and 29°260′ N and is a subtropical monsoon humid climate area. The annual average temperature is 15.9-16.6°C, the frost-free period is 242-263 days, the average annual sunshine is 1750 h and the average annual rainfall is 1200 mm. The total rainfall is 307.1 mm during the growing season. The variety is Y Liangyou 1 (super hybrid rice). The properties are shown in Table 1.

The experiment was a randomized complete block design with five treatments and three replications. The five treatments were the Control (CK), Jingzhengda slow-released fertilizer (JSCU, N 42%), Jingzhengda slow-released fertilizer and nano-carbon (JSCU+C), Stanley Slow-Released compound Fertilizer (SSRF, N-P$_2$O$_5$-K$_2$O = 20:9:11), Stanley Slow-Released compound Fertilizer and nano-Carbon (SSRF+C), respectively. Total nitrogen fertilizer dosage for every treatment was 10 kg/N, expect for CK. Phosphorus pentoxide and Potassium hydroxide were the same dosage with Stanley slow-released compound fertilizer for CK, JSCU and JSCU+C, which was replaced by the superphosphate (containing P$_2$O$_5$14%) and potassium chloride (containing K$_2$O 60%). All fertilizers were basal application in one day before transplanting and were harrowed immediately into 5 cm deep soil layer. The plot area was 25 m$^2$ and ridges of 20 cm height and 30 cm width were done between plots and plastic film were harrowed immediately into 5 cm deep soil layer. The plot area was 25 m$^2$ and ridges of 20 cm height and 30 cm width were done between plots and plastic film coated on the ridges to reduce the side water streaming. Every plot was irrigation and drainage were transplanted with 23.3×23.3 cm at June 5 and were transplanted with 23.3×23.3 cm at June 5 and harvested at September 20$^{th}$, 2010.

There were four times rainfall above 40 mm, June 5$^{th}$ to 7$^{th}$, June 15$^{th}$ to 17$^{th}$ and June 21$^{st}$ to 27$^{th}$ and August 10$^{th}$ and 15$^{th}$, respectively, during the whole rice growing season in 2010. The first three precipitations, which resulted in the runoff, were 51.9, 43.2 and 136.5 g, below the safe threshold (2.0 mg/L). The surface water for determining the total nitrogen content was sampled by the 50 mL syringe at the second (June 7$^{th}$), 4$^{th}$ (June 9$^{th}$), 7$^{th}$ (June 12$^{th}$), 14$^{th}$ (June 19$^{th}$) and 21$^{st}$ (June 27$^{th}$) day after transplanting. Six points were selected randomly in the upper surface water of every plot without disturbing the soil and subsequently injected into the plastic bottle. These
samples were back to the laboratory and digested by potassium per sulfate and determined by UV spectrophotometer. Nitrogen runoff was calculated by the multiplication of nitrogen concentration in the loss process estimated by the simulation equation from nitrogen concentration in surface water of every treatment and the runoff flux of surface water. The runoff flux was estimated by the multiplication of the depth (9.5 cm every plot) and area (25 m² every plot).

Mean chlorophyll content in the green leaves (SPAD units) was measured using a SPAD-502 m (Minolta, Japan) and averaging the recordings from the last piece of fully expanded leaves of the twenty plants of every plot in the tillering stage, booting stage, milk stage and mature stage. For determination of grain yield, all plants from every plot were harvested and grain weight and moisture percentage were recorded. Grain yield was adjusted to 12.5% moisture. Grain moisture percentage was recorded using Dickey-John multi-grain moisture tester (Dickey-John Corporation USA). Nitrogen agronomic utilization efficiency was calculated by the difference of the grain yield of nitrogen application and the grain yield of nitrogen fertilizer, which was divided by the dosage of nitrogen.

Statistical analysis of all data was determined using one-way Analysis of Variance (ANOVA) in SAS software package (Version 9.1.3, SAS Institute Inc. and Cary, NC, USA).

RESULTS

Total nitrogen concentration in surface water of paddy soil: In the experiment, total nitrogen concentration in surface water of paddy soil after applying slow-released fertilizer incorporated nano-carbon is shown in Fig. 1. The results indicated that total nitrogen concentration was increased rapidly at the 2nd day (June 7th) after fertilizer application, subsequently decreased gradually. Compared with JSRU, total nitrogen concentration under JSRU+C treatment was significantly reduced by 20.4, 37.6, 46.8 and 19.1%, at the second, 4th, 7th, 14th and 21st day (p<0.05), respectively. Similarly, under SSRF+C treatment, total nitrogen concentration in surface water of paddy soil was significantly decreased by 19.6, 48.6, 39.0 and 12.1% compared with SSRF, respectively.

Simulated equation of total nitrogen concentration in surface water of paddy soil: The relationship of total nitrogen concentration and the time after applying slow-released fertilizer in every treatment is shown in Table 2. From the model, the best-fit was no-liner model, which was exponential decreasing. According to the surface water environmental quality standards of China (GB3838-2002, 2002), the threshold of total nitrogen concentration for agricultural and landscape water body is 2.0 mg/L. However, the results showed that total nitrogen concentration was reduced to 2.0 mg/L or less for JSRU+C and SSRF+C treatments at the 10th and 6.9th day after applying slow-released fertilizer incorporated nano-carbon and at the 12.2nd and 8.7th day for JSRU and SSRF, respectively. That is, the time of N loss caused by rainfall was shorten 2.2 and 1.8 days for JSRU+C and SSRF+C and JSRU+C was better than SSRF+C.

N loss caused by rainfall and draining for sunning the fields: As noted earlier, there were four times rainfall above 40 mm and N loss happened at the first three times. As shown in Table 3, the sooner rainfall was, the more nitrogen runoff was. For SSRF, total nitrogen concentration was higher than JSRU that resulted from the faster N released rate from the third to fourth day after fertilization and the flux of nitrogen runoff was increased significantly by 28.2% after the first rainfall compared with JSRU. With the growth of rice, nitrogen in JSRU was released gradually. So, the flux of nitrogen loss for JSRU was higher than SSRF from the second rainfall. From total nitrogen runoff, there was no significant difference between JSRU and SSRF. However, the flux of total nitrogen in surface water of paddy soil after applying slow-released fertilizer incorporated nano-carbon was decreased significantly by 38.4% for JSRU+C compared with JSRU and 37.4% for SSRF+C compared with SSRF.

The main reason for N loss is rainfall and sunning the fields during the growth period of rice. In order to inhibit the excess tillers during the experiment, sunning the fields was conducted one time by draining; therefore, nitrogen loss was inevitable (Table 3). From the data, less nitrogen was run off because sunning the fields was done for a long time after fertilization. For JSRU+C, JSRU, SSRF+C and SSRF treatment, the flux of N loss was 0.20, 0.55, 0.03 and 0.06 kg/hm²,
respective. N loss was decreased by 63.6% for JSRU+C compared with JSRU and 50.0% for SSRF+C compared with SSRF. This result suggested that N loss caused by draining for sunning the fields was reduced because of nano-carbon application.

**SPAD value of rice leaves after applying slow-released fertilizer incorporated nano-carbon**: SPAD value indicates the relative amount of chlorophyll and the photosynthetic rate of the rice leaves. From Table 4, a decreased trend was presented for SPAD value under different treatments from tillering stage to mature stage and SPAD value of rice leaves after applying slow-released fertilizer was higher than CK. At tillering stage, SPAD value for JSRU+C and SSRF+C was lower than JSRU and SSRF, but the opposite trend at booting stage. The possible reason is that the number of tiller was improved after applying slow-released fertilizer incorporated nano-carbon at tillering stage (published in another paper), which resulted in the lower SPAD value, but at booting stage, there was adequate nutrients for chlorophyll synthesis as a result of the inhibited tillers caused by sunning the field and the further research is necessary.

**Grain yield and nitrogen agronomic utilization efficiency**: Grain yield and nitrogen agronomic utilization efficiency in different kinds of fertilizer treatment is shown in Table 5. The results indicated that grain yield was improved significantly after applying slow-released fertilizer incorporated nano-carbon was benefit for improving the grain yield and saving nitrogen and JSRU+C was better than SSRF+C, which may be related to the synchronization of nutrient released characteristics for JSRU+C and crop require.

Table 5 presents the effects of applying slow-released fertilizer on nitrogen agronomic utilization efficiency of rice. The results also showed that nitrogen agronomic utilization efficiency was 21.4 kg/kg N for JSRU+C and 18.4 kg/kg N for SSRF+C, which was increased by 7.9 kg/kg N compared to JSRU and 4.4 kg/kg N compared to SSRF, respectively. This suggests that it is a trend for adding nano-carbon into slow-released fertilizer.

**DISCUSSION AND CONCLUSION**

N runoff loss for farmland both affects the improvement of the nitrogen utilization efficiency, but also brings about the pollution of water body. In this experiment, total nitrogen concentration in surface water of paddy soil was increased rapidly at the 2nd day after applying slow-released fertilizer, subsequently decreased gradually and also reported by Qiu et al. (2004). According to Xiao et al. (2008), \( \text{NO}_3^-\text{N} \) leaching was decreased by applying slow-released fertilizer coated with nano-materials in the rotation of wheat-maize. In our experiment, total nitrogen concentration in surface water of paddy soil was declined from 19.1 to 46.8% for JSRU+C and from 12.1 to 48.6% for SSRF+C; the average was 31.0 and 29.8%, respectively. The results also showed that the time of N loss caused by rainfall was shorten 2.2 days for JSRU+C compared with JSRU and 1.8 days for SSRF+C compared with SSRF. That is, N runoff loss could be reduced by applying slow-released fertilizer.
incorporated nano-carbon when it was rain before the threshold of safe drainage. As we estimated, total nitrogen runoff loss was decreased by 38.4% for JSRU+C compared to JSRU and 37.4% for SSRF+C compared to SSRF. The result suggests that it is a new trend adding nano-carbon into slow-released fertilizer. The mechanism needs to further research.

Liu et al. (2008b, c, 2009) indicated that grain yields of rice, spring maize, soybean, winter wheat and vegetables were increased by 10.29, 10.93-16.74, 28.81 and 12.34-19.76% after applying fertilizer adding nano-materials. As reported by Liu et al. (2007), nano-materials could promote germination and rooting early for rice seeds and seedlings and the growth of rice at tillering stage was affected obviously by nano-composites. Our results indicated that SPAD value of rice leaves at booting stage, the grain yield and nitrogen agronomic utilization efficiency was increased after applying slow-released fertilizer incorporated nano-carbon and ratio of saving nitrogen of per 1 kg rice grain was increased by 10.1% for JSRU+C compared to JSRU and 5.3% for SSRF+C compared to SSRF. The possible reasons are:

- As a low-lighted and non-conductive modified carbon, nano-carbon could detach N from NH$_3^+$ and thus H$^+$ was released, which promoted the plant to absorb the water of the soil and the nutrients in water and improve the photosynthesis.
- In the soil, HCO$_3^-$ is one of ion adjusting the balance between anion and cation, which is absorbed directly by plant root and promotes the photosynthesis of leaves.

EC value of the soil is improved by 30% when nano-carbon dissolved in the soil water, which promoted the composition of HCO$_3^-$, N, P and K are flowed into the plant and transformed into starches and proteins with absorbing HCO$_3^-$ in plant root. So, nano-carbon is considered the biological pump for the plants to absorb nutrients and water (Ma et al., 2009). As reported by Liu and Liao (2008a), the activity of water after adding nano-materials was increased and N, P and K were absorbed into the plants with the absorbing of water, thus the production was also increased.

From the experiment, total nitrogen concentration in surface water of paddy soil was increased rapidly at the 2nd day after applying slow-released fertilizer, subsequently decreased gradually. The time of N loss caused by rainfall was shorten 2.2 days for JSRU+C compared with JSRU and 1.8 days for SSRF+C compared with SSRF. The results also showed that SPAD value of rice leaves at booting stage, the grain yield and nitrogen agronomic utilization efficiency was increased after applying slow-released fertilizer incorporated nano-carbon and JSRU+C was better than SSRF+C.

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